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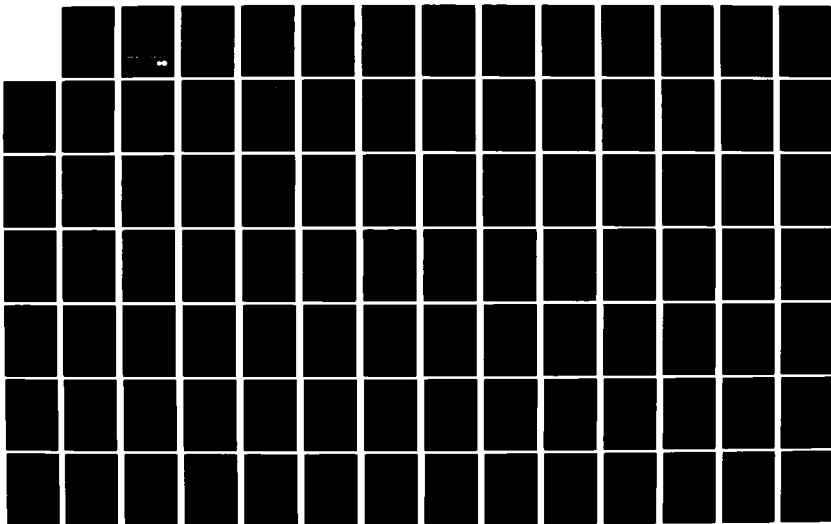
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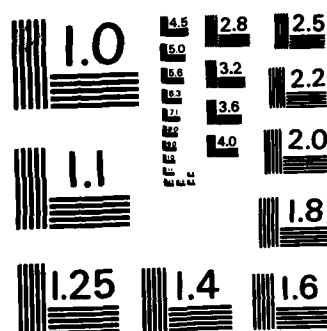
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INTERIM TECHNICAL REPORT

**RECOMBINATION AND CHEMICAL REACTIONS IN
DENSE IONIZED GASES**

**By
M. R. Flannery**

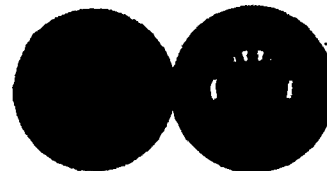
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**GEORGIA INSTITUTE OF TECHNOLOGY
A UNIT OF THE UNIVERSITY SYSTEM OF GEORGIA
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A new and basic theory of ion-ion recombination in a dense gas has been developed from basic microscopic principles. The recombination rate is provided as a function of gas density, ion density and time. Various simplified treatments of ion-ion recombination are also presented. Research progress accomplished between January 1 - December 1981 is fully documented in seven published papers which appear as Appendices A - G of this report. <i>←</i>		

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Abstract

The research performed under AFOSR grant no. AFOSR-80-0055 during the period January 1, 1981 - December 31, 1981 is reported. The theory formulated and results obtained are fully documented by seven published papers which appear in Appendices A - G of this report and which represent a complete account of the work performed during the 1981 year. In particular, a new and basic theory of ion-ion recombination in a dense gas has been developed from basic microscopic principles and is fully described in Appendix F.



A

1. Refereed Research Publications under AFOSR Grant

1.1 January 1, 1980 - December 31, 1980

1. "Charge-Transfer in Three-Body Ion-Ion Recombination at Low Gas Densities", Int. J. Quant. Chem.: Quant. Chem. Symp. 14, 477-482 (1980).
2. "Ion-Ion Recombination in ($X^+ + Y^- + X$) Systems at Low Gas Densities: I. Symmetrical Resonance Charge-Transfer Contribution", J. Phys. B: Atom. Molec. Phys. 13, 3649-3664 (1980).
3. "Three-Body Recombination of Rare-Gas Atomic Ions X^+ with F^- in a Low-Density Gas X", with T. P. Yang, J. Chem. Phys. 73, 3239-3245 (1980).
4. "Theoretical Treatment of Collisions of Rydberg Atoms with Neutral Atoms and Molecules. The Semiquantal, Impulse and Multistate-Orbital Theories", Phys. Rev. A 22, 2408-2429 (1980).
5. "Ion-Ion Recombination in ($X^+ + Y^- + Z$) Systems at Low Gas Densities. II. Elastic Ion-Neutral Collisions", J. Phys. B: Atom. Molec. Phys. 14, 915-934 (1981).

Separate copies of reprints of all of these publications (1) - (6) have already been forwarded during the course of the 1981-year and were fully documented in the interim report for the previous year (1980).

1.2 January 1, 1981 - December 31, 1981

6. "Thermal Collisions of Rydberg Atoms with Neutrals", J. Phys. B: Atom. Molec. Phys., L657-663 (1980).
7. "Vibrational Deactivation of Oxygen Ions in Low Velocity $O_2^+(X \ ^3\Pi_g, v=1) + O_2(X \ ^3\Sigma_g^-, v=0)$ Collisions", with T. F. Moran, K. J. McCann, M. Cobb and R. F. Borkman, J. Chem. Phys. 74, 2325-2330 (1981).

8. "Ion-Ion Recombination as a Function of Ion and Gas Densities", Chem. Phys. Letts. 80, 541-546 (1981).
9. "Exact Closed Form Solution of the Generalized Debye-Smoluchowski Equation", Phys. Rev. Letts. 47, 163-166 (1981).
10. "Ion-Ion Recombination in Dilute and Dense Plasmas", Int. J. Quant. Chem.: Quant. Chem. Symp. 15, 715-727 (1981).
11. "Theory of Ion-Ion Recombination", Phil. Trans. Roy. Soc. (London) A 304, 447-497 (1982).
12. "Analytical Solutions of the Debye-Smoluchowski Equation for Geminate and Homogeneous Recombination and for Fluorescence Quenching", Phys. Rev. A 25, 3403-3406 (1982).

Copies of all of the above papers #6-12 appear as Appendices A - G of this interim report. These papers represent the research work performed during 1981, under the present AFOSR grant.

2. Papers Presented at Scientific Meetings

1. "Basic Microscopic Theory of Ion-Ion Recombination", Invited Lecture presented at International Symposium on Atomic, Molecular and Solid State Theory, Florida, March 9-14, 1981
2. "Basic Microscopic Theory of Neutralization and of Chemical Reactions in Dense Gases", Special Long Paper (30 mins.) delivered at 34th Annual Gaseous Electronics Conference, Boston, Mass., October 20-23, 1981.
3. "Theory of Chemical Reactions in Dense Gases", delivered at Thirteenth Annual Meeting of the Division of Electron and Atomic Physics (APS/DEAP), New York, December 3-5, 1981.

3. Special Highlights: New Theoretical Developments in Present Research

A new and basic theory of ion-ion recombination as a function of gas density N has been developed (M. R. Flannery, Phil. Trans. Roy. Soc. A) from basic microscopic principles. A key equation for the distribution in phase space of ion pairs has been derived together with an expression for the resulting recombination coefficient α . Further development of the theory leads to interesting insights to a full variation with N of α , which is shown to yield the correct limits at low and high N . The recombination rate α is determined by the limiting step of the rate α_{RN} for ion reaction and of the rate α_{TR} for ion transport to the reaction zone. An accurate analytical solution of the time-dependent Debye-Smoluchowski equation which is a natural consequence of this theory, has been provided, for the first time, for transport/reaction under a general interaction V in the cases of an instantaneous reaction ($\alpha_{RN} \gg \alpha_{TR}$) and of a finite rate ($\alpha_{RN} \sim \alpha_{TR}$) of reaction within a kinetic sink rendered compressible via variation of gas density. Expressions for the transient recombination rates $\alpha(t)$ have then been derived and illustrated. The exhibited time dependence lends itself to eventual experimental verification at high N .

A theory which investigates the variation of α with ion density N^\pm has also developed. Here the ion-ion interaction V can no longer be assumed ab-initio to be pure Coulomb but is solved self-consistently with the recombination. Recombination rates for various systems have been illustrated as a function of N via a simplified method for the reaction rate. Finally, two theoretical procedures for the solution of the general phase-space ion distributions have been proposed.

Appendix A

Thermal Collisions of Rydberg Atoms with Neutrals, J. Phys. B: Atom.
Molec. Phys., L657-663 (1980).

LETTER TO THE EDITOR

Thermal collisions of Rydberg atoms with neutrals

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Received 17 July 1980

Abstract. A new theoretical method outlined here for an important inelastic mechanism based on $A-B^+$ encounters in $A-B(n)$ thermal collisions indicates a substantial contribution to l -changing transitions which therefore cannot be viewed as proceeding via $(e-A)$ encounters alone. Recent descriptions of l -changing thermal collisions which are based on an $(e-A)$ impulse treatment appear defective in that they disregard certain impulse validity criteria and yield results which greatly exceed the upper limit specified by the basic impulse expression, and do not recognise the above important inelastic mechanism associated with the non-inertiality of the core.

In the collision process,

$$A(i) + B(n) \rightarrow A(j) + \begin{cases} B(n') \\ B^+ + e \end{cases} \quad (1)$$

between an incident atom (or molecule) A and a target atom B initially in a highly excited state with principal quantum number n , *energy and momentum changes* to the Rydberg electron (labelled 1) can be assumed, under certain conditions (see Flannery 1980 and below), to occur via a collision of 1 with the projectile A (labelled 3). A (1-3) inelastic encounter includes the additional possibility of simultaneous $(i \rightarrow j)$ transitions in the internal state of A . Based on this premise, a semiquantal treatment was developed (Flannery 1970, 1973) mainly for the ionisation channel in (1) and was recently derived (Flannery 1980) from the basic quantal impulse expression (cf Coleman 1969) in which the wavefunction for the ejected electron is replaced by a plane wave.

The three basic assumptions within the impulse approximation to $A-B(n)$ collisions become fully transparent from a derivation (Flannery 1980) based on the two-potential formula and they are as follows.

(i) The interactions V_{12} and V_{32} of 1 and 3 with the core B^+ (labelled 2) are switched off during the (1-3) collision time and V_{12} is invoked only to establish the initial and final quantal states of the target system.

(ii) The distortion of the motion of the projectile 3 in the field V_{32} due to the core 2 is neglected when interacting with both 2 and with the Rydberg electron 1.

(iii) Inelastic transitions in B are prohibited in *direct* ($A-B^+$) encounters.

Although (i)-(iii) may be justified for many kinds of $A-B(n)$ direct collision processes at sufficiently high n and collision speeds $v_3 \gg v_1$, the orbital speed of the Rydberg electron, conditions (ii) and (iii) can be seriously violated, particularly when $v_1 \ll v_3$. Various implications of (i)-(iii), discussed below, cast serious doubts on the overall validity of various models recently proposed (Matsuzawa 1979 and references

therein, Hickman 1979, de Prunelé and Pascale 1979) for angular momentum l -changing and quenching collisions between $B(nl)$ and rare-gas atoms at thermal energies (when $v_1 \gg v_3$), a subject of great current experimental interest and activity (Hugon *et al* 1979, 1980 and references therein, Gallagher *et al* 1977). Moreover, the models are based on further simplification such as a Born or δ -function reduction within the basic impulse expression and, as such, entail additional validity criteria. The models yield results greatly in excess of the actual upper limit imposed by the basic impulse expression (cf Flannery 1980). Also they neglect the effect of thermal (2-3) collisions which are, in fact, important.

(iv) Although not essential to the impulse treatment, 'on-the-energy-shell' (1-3) encounters in all applications to $A-B(n)$ collisions are tacitly assumed, a procedure valid only in the high-energy or weak-binding limit.

Assumptions (i)-(iii) above imply important conditions of special significance to $A-B(nl)$ thermal collisions.

Condition A. Switching off the core interactions ($V_{12} + V_{32}$) during the (1-3) collision time τ_c implies that energy can be controlled only to within an imprecision $\Delta E_1 \sim \hbar/\tau_c$ during the collision, i.e. the energy dependence of the electron-1-projectile-3 cross section σ_{13} must not exhibit too rapid a variation as occurs, for example, in the neighbourhood of an electron-atom resonance in which a negative ion A^- is temporarily formed, or in the vicinity of a Ramsauer minimum evident for e-Ar, Kr and Xe scattering. This implication is ignored by Matsuzawa (1979) in his resonance and l -changing studies, by Hickman (1979) and by others (e.g. de Prunelé and Pascale). When $v_1 \gg v_3$, $\tau_c \sim A_1 n$ (au) where $A_1(a_0)$ is the (e-A) interaction distance such that during τ_c the energy imprecision $\Delta E_1 \sim (A_1 n)^{-1}$ au is comparable with the small impact energy $\frac{1}{2}v_1^2$. For $v_3 \gg v_1$, however, $\Delta E_1 \sim v_3/A_1$ which is very much less than $\frac{1}{2}v_3^2$ the relative energy over which σ_{13} generally varies slowly.

Condition B. The momentum P transferred (impulsively) to 1 during the collision time τ_c must be very much greater than the momentum imparted to 1 during the same time via the force F due to its interaction V_{12} with the core, i.e.

$$P \gg \int_{\tau_c} F dt \approx |\langle \phi_{nl} | -\nabla V_{12} | \phi_{nl} \rangle| \tau_c \approx \frac{\tau_c}{n^3(l+\frac{1}{2})} \quad (2a)$$

where ϕ_{nl} is the electronic wavefunction for the Rydberg electron with orbital period $T_n \sim n^3$ au for each l such that

$$\tau_c \ll T_n(l+\frac{1}{2})P. \quad (2b)$$

If V_{12} varies sufficiently slowly (but need not be necessarily small!) over the range A_1 of the collision interaction V_{13} , such that the force $F (= -\nabla V_{12})$ due to the core is small in comparison with the impulsive force $(-\nabla V_{13})$ due to the Rydberg electron-projectile interaction, then (2) is satisfied; in this sense V_{12} can be regarded as 'quasiclassical'.

For ionising collisions, $P \gg n^{-1}$, then $\tau_c \ll T_n$ for circular orbits ($l \sim n$) and $\tau_c \ll T_n/n$ for highly eccentric orbits ($l \sim 0$). Hence, the requirement $\tau_c \ll n^2$ covers electron ejection from all orbits. For non-ionising collisions, P by (2) cannot become arbitrarily small, which could occur for quasi-elastic or l -changing collisions. At thermal energies, the electron speed $v_1 \sim n^{-1}$ au is greater than the incident speed $v_3 \sim 10^{-4}$ au of A for most n of interest, and the collision time $\tau_c \sim A_1 n$ for e-rare-gas atom scattering (where $A_1 \sim (1-7)a_0$) such that (2) implies that $P \gg A_1/n^2(l+\frac{1}{2})$. The angular momentum

change (for fixed n) due to (e-A) impulsive encounters at R_{12} from B^+ must satisfy

$$\Delta L \sim P(R_{12}) \sim \frac{1}{2}P[3n^2 - l(l+1)] \gg \frac{1}{2}A_1[3n^2 - l(l+1)]/n^2(l+\frac{1}{2}) \quad (3)$$

which is, in general, fulfilled only at the highest initial l when the permitted $\Delta L \gg A_1/(l \sim n)$. Small initial l require large changes $\Delta L \gg A_1$ for validity of the impulse model (since then the momentum imparted by the core on the highly elliptical orbits becomes considerably strengthened over that for circular orbits). The above considerations are absent in any previous l -changing study (Matsuzawa 1979, Hickman 1979, de Prunelé and Pascale 1979).

Condition C. Since the distortion of V_{32} on the projectile 3 is neglected, the contribution to the basic impulse T -matrix element from (2-3) collisions is real and is non-vanishing only for elastic transitions in the target (Flannery 1980), the cross section for all elastic and inelastic events is, from the optical theorem, given in both the basic impulse expression and the semiquantal treatment by (Flannery 1980),

$$\sigma_{13}^{\text{tot}}(v_3) = \frac{1}{v_3} \int |g_i(k_1)|^2 [v_{13} \sigma_{13}^T(v_{13})] dk_1 \quad (4)$$

where $|g_i|^2$ is the probability that the Rydberg electron has momentum k_1 , where σ_{13}^T is the total cross section for all elastic and inelastic (1-3) collisions at relative speed v_{13} and where v_3 is the speed of the projectile A in the (A- B^+) centre-of-mass reference frame. This cross section (4) is an *upper limit* to any collision process satisfying specific criteria for the validity of the impulse approximation and states that the rate ($v_3 \sigma_{13}^{\text{tot}}$) for all A-B(n) elastic and inelastic processes is essentially limited to the total rate of free Rydberg e-A collisions. For $v_1 \gg v_3$, as in thermal collisions, then

$$\sigma_{13}^{\text{tot}}(v_3) = \langle v_1 \sigma_{13}(v_1) \rangle / v_3 \approx \bar{v}_1 \sigma_{13}(v_1) / v_3 \quad (5)$$

where the average is taken over the distribution in orbital speed v_1 of the Rydberg electron. de Prunelé and Pascale (1979) (and also Matsuzawa 1979) have correctly conjectured that (5) can be deduced from the semiquantal formulation of A-B(n) collisions. However, many treatments (Matsuzawa 1979, Hickman 1979) of l -changing collisions alone, which are simple derivatives of the basic impulse expression, yield results much larger than (4) or (5) in violation of the impulse upper limit. Curiously enough, their apparent agreement with experiment does not substantiate the assertion that l -changing collisions at thermal energies originate solely from slow Rydberg e-atom encounters. That the (1-3) impulse upper limit yields values much lower than experiment (see table 1 and semiquantal results calculated by de Prunelé and Pascale (1979)) simply infers that an important mechanism, discussed below and based on 2-3 encounters, has not been acknowledged.

Condition D. Assumption (ii) based on the neglect of distortion of V_{32} on 3 while interacting with 1 implies that 1 and 2 behave as separate and as independent scatterers. This is valid provided (a) that the (1-2) separation $R_{12} \approx n_2 a_0 \gg A_{1,2}$, the scattering lengths or amplitudes for (1-3) and (2-3) collisions, and (b) that the reduced wavelength λ_{13} for (i -3) relative motion is very much less than R_{12} , so that A_1 is not affected by the presence of A_2 (and vice versa). In general, $\lambda_{13} \ll n^2$ for high impact speeds $v_3 \gg v_1$, and for thermal-energy collisions when $v_1 \gg v_3$ such that $\lambda_{13} \sim v_1^{-1} \approx n$; and $A_{1,2} \ll n^2$. Moreover, for (2-3) collisions at thermal energies $\lambda_{23} \sim k_3^{-1} \approx 10^{-1}$ (see table 1). Hence

$R_{12}^2 \gg \lambda_{i3} A_i$ such that multiple scattering can be neglected. Curiously enough, condition D is the one most easily satisfied in A-B(n) collisions and is the only condition of all here which receives consideration in previous studies.

Condition E. At thermal energies distortion of 3 due to the core 2 cannot be ignored, as in assumption (ii), and the cross section for B⁺-A elastic thermal collisions are large, about 10^3 \AA^2 (cf Dalgarno 1970). The impulse expression customarily adopted (cf Coleman 1969) must be appropriately generalised. The result (Flannery 1980) involves a nine-dimensional integral for the T matrix rather than the usual three dimensional integral, and appears valuable only in promoting deeper understanding. This condition of undistortion is closely related to D.

Condition F. However, the impulse model focuses attention on the (1-3) collision, whether distorted by V_{32} or not and as such does not contain any inelastic electronic transitions due to direct (2-3) encounters (assumption (iii)). Effective allowance for inelastic transitions via (2-3) collisions due to the non-inertiality of the target core 2 can be readily obtained (Flannery 1980). Let the impulse procedure treat the (1-3) encounter, for which purpose it has been designed. Then in the absence of the interaction V_{13} between the incoming projectile 3 and the Rydberg electron 1, the Hamiltonian for the complete A-B(n) system of reduced mass M_{AB} is

$$H = -\frac{\hbar^2}{2M_{12}} \nabla_r^2 - \frac{\hbar^2}{2M_{AB}} \nabla_R^2 + V_{23}(\mathbf{R}') - \frac{e^2}{r} \quad (6)$$

where the vector \mathbf{R}' of 3 relative to 2, in terms of its position \mathbf{R} relative to the (1-2) centre-of-mass and \mathbf{r} the vector separation of (1-2) of reduced mass M_{12} is given by

$$\mathbf{R}' = \mathbf{R} + (M_1/M)\mathbf{r} \quad M = M_1 + M_2 \quad (7)$$

where M_i is the mass of particle i . The (2-3) interaction can then be expanded as

$$V_{23}(\mathbf{R}') = V_{23}(\mathbf{R}) + (M_1/M)\mathbf{r} \cdot \nabla V_{23}(\mathbf{R}) + \dots \quad (8)$$

The full scattering solution for H can be expanded in terms of the target basis $\{\phi_n(\mathbf{r})\}$, and a hierarchy of quantal and semiclassical approximations exist (to various degrees of sophistication) which are based on matrix elements,

$$\begin{aligned} V_{ji}(\mathbf{R}) &= \langle \phi_j(\mathbf{r}) | V_{23}(\mathbf{R}') | \phi_i(\mathbf{r}) \rangle \\ &= V_{23}(\mathbf{R}) \delta_{ji} + (M_1/M) \langle \phi_j(\mathbf{r}) | \mathbf{r} | \phi_i(\mathbf{r}) \rangle \cdot \nabla V_{23}(\mathbf{R}) + \dots \end{aligned} \quad (9)$$

In particular, Flannery (1980) has shown in the sudden limit to a semiclassical analysis, when the exponential phase factors ($i\epsilon_{fn}t/\hbar$) can be ignored, (i.e. the collision time t is assumed small in comparison with the time \hbar/ϵ_{fn} for transitions between highly excited levels n and f with energy separation ϵ_{fn} or else the important levels n and f are assumed degenerate as in l -changing transitions), that the differential cross section for ($i \rightarrow f$) transitions in the target B via A-B⁺ (2-3) encounters is

$$\left(\frac{d\sigma_f}{d\Omega} \right) = |B_f(\rho, t \rightarrow \infty)|^2 \left(\frac{d\sigma_{23}}{d\Omega} \right) \quad (10)$$

where $(d\sigma_{23}/d\Omega)$ is the differential cross section for (2-3) elastic scattering and where

$$B_f(\rho, t \rightarrow \infty) = \left\langle \phi_f(\mathbf{r}) \left| \exp \left[i \left(\frac{M_1}{\hbar M} \right) \mathbf{r} \cdot \int_{-\infty}^{t \rightarrow \infty} \nabla V_{23}(\mathbf{R}(t)) dt \right] \right| \phi_i(\mathbf{r}) \right\rangle \quad (11)$$

is the probability amplitude at impact parameter ρ for the $i \rightarrow f$ transition. Since

$(-\nabla V_{23})$ in (11) is the force on 2 due to 3, the 'impulse'

$$\int_{-\infty}^{\infty} \mathbf{F}_{23} dt = M_{23}(\mathbf{v}'_{23} - \mathbf{v}_{23}) = M_2 \mathbf{v} \quad (12)$$

is the momentum $M_2 \mathbf{v}$ transferred to the core 2, where \mathbf{v}_{23} and \mathbf{v}'_{23} are the initial and final velocities of the (2-3) collision system with reduced mass M_{23} . Thus, the probability of the $(i \rightarrow f)$ transition is

$$|B_f(\rho, t \rightarrow \infty)|^2 = |\langle \phi_f(r) | \exp(iM_{12} \mathbf{v} \cdot \mathbf{r}) | \phi_i(r) \rangle|^2 \quad (13)$$

the absolute square of the inelastic atomic form factor which, when summed over all final states, yields unity. A simple interpretation of (13), based on the recognition that the Rydberg electron which is bound to the core at rest before the collision, finds itself relative to a moving core after the collision, can be provided (Flannery 1980). Account of the translational factor so introduced (as in hydrogenic travelling orbitals ϕ_T) and the sudden approximation $|\langle \phi_T | \phi_i \rangle|^2$ for the transition probability yields (13).

The total cross section for all elastic and inelastic transitions based on (2-3) collisions from (10) and (13) is given by

$$\sigma_{23}^{\text{tot}}(v_{32}) = \sigma_{23}^{\text{el}}(v_{32}) \quad (14)$$

which is therefore an upper limit. A highly accurate representation of the integral elastic cross section is provided by the semiclassical expression (see Dalgarno 1970),

$$\sigma_{23}^{\text{el}}(v_{32}) = 1.0688 \times 10^3 \left(\frac{\alpha M_{AB}}{k_3} \right)^{2/3} a_0^2 \quad (15)$$

where αa_0^3 is the polarisability of 3 and where $k_3(\text{au})$ is the momentum of the (A^+-B) system with reduced mass $M_{AB}(\text{amu})$. A preliminary assessment based on the upper limits (5) and (15) can now be made.

The table illustrates (5) and (15) for thermal (520 K) collisions of Rb(15F) with rare gases RG(He, Ne, Ar, Kr and Xe) for which $v_1 \gg v_3$. The (e-RG) cross section $\sigma_{13}(v_1)$ were obtained from the phaseshifts of Yau *et al* (1979, 1980) and were so normalised as to reproduce measurements (where available) of the scattering length A_1 (since for He, Ne and Ar the calculated scattering lengths were 13% lower, 11% lower and 40% higher than the respective measurements (cf Yau *et al* 1979, 1980)). The first value in the range σ_{13}^{tot} arising from (1-3) elastic collisions corresponds to $\sigma_{13} = 4\pi A_1^2$ at zero

Table 1. Maximum cross sections (\AA^2) for Rb(15F)-rare-gas (RG) collisions at 520 K based on the sum of (e-RG) elastic encounters with cross section σ_{13}^{tot} and on (Rb $^+$ -RG) elastic encounters with cross section σ_{23}^{tot} . The relative speed, momentum and polarisability of the incident RG atom are v_3 , k_3 and α respectively. The measurements (Exp) are taken from table 1 of Hugon *et al* (1979).

RG	$v_3(10^{-4} \text{ au})$	$k_3(\text{au})$	$\alpha(a_0^3)$	$\sigma_{23}^{\text{tot}}(\text{\AA}^2)$	$\sigma_{13}^{\text{tot}}(\text{\AA}^2)$	$(\sigma_{13}^{\text{tot}} + \sigma_{23}^{\text{tot}})\text{\AA}^2$	Exp(\AA^2)
He	7.757	5.405	1.384	2.95 [†]	(4.28 ² -4.91 ²)	(7.23 ² -7.86 ²)	(8.1 ± 1.6) ²
Ne	3.754	11.17	2.666	7.41 ²	(5.63 ¹ -1.74 ²)	(7.98 ² -9.15 ²)	—
Ar	2.907	14.42	11.07	2.27 ³	(1.82 ³ -3.52 ²)	(4.09 ³ -2.62 ³)	(2.5 ± 0.5) ³
Kr	2.332	17.98	16.74	3.47 ³	(1.78 ⁴ -3.66 ³)	(2.13 ⁴ -7.13 ³)	—
Xe	2.108	19.86	27.26	5.13 ³	(6.80 ⁴ -1.00 ⁴)	(7.31 ⁴ -1.51 ⁴)	(2.0 ± 0.7) ⁴

[†] 2.95² = 2.95 × 10².

Appendix B

Vibrational Deactivation of Oxygen Ions in Low Velocity $O_2^+(X\ ^3\Pi_g, v=1)$
+ $O_2(X\ ^3\Sigma_g^-, v=0)$ Collisions, with T. F. Moran, K. J. McCann, M. Cobb
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Vibrational deactivation of oxygen ions in low velocity $O_2^+(X^2\Pi_g, v=1) + O_2(X^3\Sigma_g^-, v=0)$ collisions

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The deactivation of $O_2^+(X^2\Pi_g, v=1)$ ions in collisions with $O_2(X^3\Sigma_g^-, v=0)$ molecules has been examined using multistate impact parameter eikonal and orbital treatments. Cross sections for the formation of various product states in the charge exchange and direct scattering channels have been computed for ions with 0.5 to 8.0 eV c.m. kinetic energies. The relative probabilities for forming products in given vibrational states at the higher kinetic energies are similar for the eikonal and orbital approaches. At energies below several eV it is necessary to employ the multistate orbital treatment which takes explicit account of the strong ion-molecule scattering. Cross sections for reaction channels leading to de-excitation and/or excitation of the product $O_2^+(X^2\Pi_g, v=1)$ ions have been computed for both charge exchange and direct scattering processes. The channels leading to vibrationally deactivated $O_2^+(X^2\Pi_g, v=0)$ product ions are strongly favored at low velocities over the excitation processes in the charge exchange as well as in the direct scattering channels.

INTRODUCTION

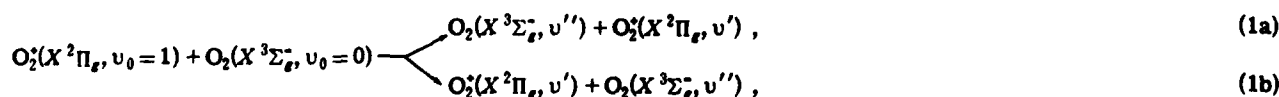
As more information is assembled on the reactions of ions with neutral molecules, it is becoming evident that reaction rate constants for many processes depend strongly on the internal energy of the reactants.¹ The magnitude of the cross sections for charge transfer reactions of atomic ions with neutral molecules varies widely,^{2,3} depending on whether the reactant ions occupy the ground or excited electronic state. Likewise, cross sections for collision induced dissociation of various molecular ions depend^{4,5} on the vibrational and/or electronic state distributions of the ions. The influence of the neutral target molecule vibrational state has been examined^{6,7} in reactions of O^+ and Ne^+ ions with $N_2(X^1\Sigma_g^+, v)$. The investigation by Albritton *et al.*^{1,8} has shown that the rearrangement reaction of $O_2^+(X^2\Pi_g, v)$ with CH_4 producing $CH_3O_2^+$ and CH_3^+ is strongly dependent on the $O_2^+(X^2\Pi_g, v)$ vibrational state. This drift tube experiment^{1,8} has clearly demonstrated that a small amount of $O_2(X^3\Sigma_g^-, v=0)$ gas, added to the Ar buffer gas, effectively quenches the hydrocarbon rearrangement re-

action due to vibrational deactivation of $O_2^+(X^2\Pi_g, v=1)$ ions by charge exchange processes which result in the formation of the much less reactive $O_2^+(X^2\Pi_g, v=0)$ ions.

Previous theoretical investigations have examined charge transfer reactions in the symmetric $O_2^+-O_2$ system and have shown that vibrational excitation of the products occurs with high probability for ions in the keV range.⁹⁻¹¹ Vibrational excitation processes are efficient in both the direct as well as the exchange channels due to strong coupling between these energy degenerate channels.^{10,11} Differential and integral charge transfer and direct scattering cross sections in the hundred eV range are adequately represented by the multistate eikonal treatment, but there is a lack of detailed information on these processes for the oxygen system at low (eV range) kinetic energies. The purpose of this investigation is to examine $O_2^+(X^2\Pi_g, v=1) + O_2(X^3\Sigma_g^-, v=0)$ collisions in an effort to understand the competition between the various ionic excitation and de-excitation channels as a function of reactant ion kinetic energy.

RESULTS AND DISCUSSION

The multistate impact-parameter treatment has been used to examine vibrational transitions occurring in the symmetric ion-molecule system



where charge transfer reactions predominate. In Reaction (1a), the incident molecular $O_2^+(X^2\Pi_g, v_0=1)$ ions initially in level v_0 capture an electron to form fast neutral $O_2(X^3\Sigma_g^-, v'')$ molecules in vibrational level v'' , while in the direct channel (1b) incident molecular ions are scattered with the fast product ions in level v' . Each of the charge transfer channels (1a) is degenerate in energy with a corresponding direct channel (1b) which leads to strong coupling between the charge transfer and direct processes in this symmetric ion-molecule system. Application of the multistate treatment to these reactions is made in the following sections.

Multichannel eikonal treatment

The wave function which represents the time-dependent response of the internal motions of the system under the influence of the mutual interaction $V(R, r)$ is described by

$$\psi_i(r, R) = \sum_{a,D,X} \sum_n C_n^a(\rho, Z) \psi_n^a(r) \exp[-(iE_n^a t)] , \quad (2)$$

where $\psi_n^a(r)$ are a complete set of molecular eigenfunctions (with electronic, vibrational, and rotational parts) describing the unperturbed Hamiltonian \mathcal{H}_0 for the iso-

lated system at infinite center-of-mass separation R with eigenenergies E_α^α . The index α denotes whether the labeled quantities refer to direct channels D or to charge exchange channels X . The quantity r denotes the collection of internal coordinates on each center. Substitution of the wave function (2) into the time-dependent Schrödinger equation results¹² in the following set of coupled equations for the transition amplitudes $C_m^\alpha(t)$:

$$i\partial C_f^\alpha(\rho, t)/\partial t = \sum_m V(R) P_{fm} C_m^\alpha(\rho, t) \exp(i\epsilon_{fm}t), \quad f=1, 2, \dots, N, \quad (3)$$

which are solved numerically subject to the boundary condition that the direct channel i is initially populated, i.e., $C_m^D(\rho, -\infty) = \delta_{mi}$, $C_m^X(\rho, -\infty) = 0$. Matrix elements P_{fm} are equal to $F(v_i', v_m'')F(v_m', v_f')$, where $F(v_i', v_m'')$ is the vibrational overlap for the $O_2^+(X^2\Pi_g, v=1) \rightarrow O_2(X^3\Sigma_g^-, v'')$ transition. When α denotes X in Eq. (3), $\bar{\alpha}$ refers to D and vice versa. Differences ϵ_{if} in the internal energies between initial and final states of the system are given by $E_i^\alpha - E_f^{\bar{\alpha}}$. The equation used to compute the scattering amplitude in the c.m. frame is¹³

$$f_{fi}^\alpha(\theta, \phi) = \left\{ -\frac{ik_i}{2\pi} \right\} \int \exp[i(\mathbf{K} \cdot \mathbf{R} + m_{if}\Phi)] \times \exp(i\epsilon_{if}Z/\hbar v_i) (\partial C_f(\rho, Z)/\partial Z) d\mathbf{R}, \quad (4)$$

where the incident velocity is $\mathbf{v}_i = \hbar \mathbf{k}_i/\mu$, the momentum change \mathbf{K} during the collision is $\mathbf{k}_i - \mathbf{k}_f$ with the final momentum vector \mathbf{k}_f directed along (θ, ϕ) , and m_{if} is the change in azimuthal quantum number which is taken to be zero for the reactions under investigation here. The ion-molecule separation vector \mathbf{R} has spherical components (ρ, Φ, Z) , where ρ is the impact parameter. For high energy collisions, a straight line trajectory is adequate with

$$\mathbf{R}(t) = \rho + \mathbf{v}_i t, \quad (5)$$

where the velocity is taken to be along the Z axis and is perpendicular to the impact parameter. In this situation the solution of Eq. (4) is simplified by noting that for heavy-particle collisions the Z component of the momentum transfer can be approximated by

$$K_z = k_i - k_f \cos \theta = k_i - k_f, \\ = (\epsilon_{fi}/\hbar v_i) [1 + \epsilon_{fi}/2\mu v_i^2 + \dots]. \quad (6)$$

Equation (4) can be simplified¹³ to

$$f_{fi}^\alpha(\theta, \phi) = -k_i i^{\Delta+1} e^{i\Delta\phi} \times \int_0^\infty J_\Delta(K'\rho) [C_f^\alpha(\rho, \infty) - \delta_{if}] \rho d\rho \quad (7)$$

by performing the Φ integration. In Eq. (7), δ_{if} is the Kronecker delta function and J_Δ are Bessel functions of integral order $\Delta = m_{if}$, and $K' = (K^2 - K_\perp^2)^{1/2}$ is the momentum transfer perpendicular to the trajectory. From these scattering amplitudes given by Eq. (7), the differential cross section is

$$\sigma_{fi}^\alpha(\theta) = 2\pi \frac{k_f}{k_i} |f_{fi}^\alpha(\theta, \phi)|^2. \quad (8)$$

Integrating Eq. (8) over angle yields the integral cross section $Q_{fi}^\alpha(v_i)$ given by the equation

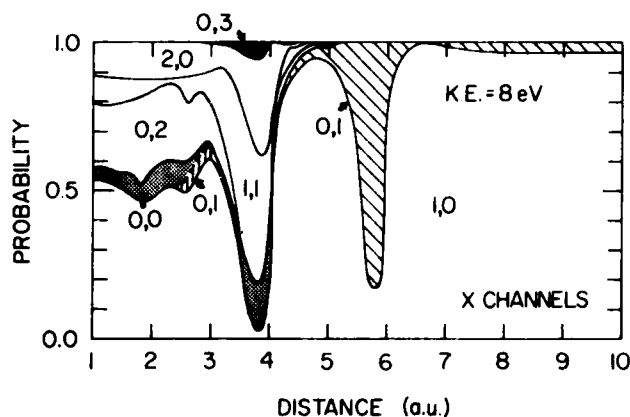


FIG. 1. Relative probabilities (eikonal method) for formation of specific product channels in 8.0 eV c.m. $O_2^+(X^2\Pi_g, v=1) + O_2(X^3\Sigma_g^-, v''=0)$ charge exchanging collisions as a function of impact parameter distance in atomic units. The numbers associated with each area denote the vibrational quantum numbers of the respective $O_2^+(X^2\Pi_g, v')$ and $O_2(X^3\Sigma_g^-, v'')$ reaction products.

$$Q_{fi}^\alpha(v_i) = \int_{-1}^1 \sigma_{fi}^\alpha(\theta) d(\cos \theta) \\ = 2\pi \int_0^\infty |C_f(\rho, \infty) - \delta_{if}|^2 \rho d\rho. \quad (9)$$

The interaction matrix elements $V(R)$ necessary to describe Reactions (1) are those used previously¹¹ for this system and they are considered sufficiently accurate and suitable for this study. Energy defects and accurate vibrational overlaps for the respective transitions have been obtained from previously published¹⁴ wave functions which were constructed using RKR techniques.¹⁴ For the reactions of $O_2^+(X^2\Pi_g, v=1)$ ions with $O_2(X^3\Sigma_g^-, v=0)$ molecules, the dominant product channels are those with small energy defects and favorable vibrational overlaps. Product channels with small energy defects are 1, 0; 0, 1; 0, 0; 0, 2; 1, 1; 2, 0; 0, 3 (the vibrational level v' of the production is denoted by the first number and the vibrational level v'' of the product neutral as the second number in the pair).

The computation of the cross sections for charge transfer and direct scattering processes requires solution of the coupled differential equations (3). These coupled differential equations are solved numerically by the Burlisch-Stoer rational extrapolation technique.¹⁵ Transition amplitudes $C_m^\alpha(\rho, \infty)$ determined as a function of ρ from the multistate coupled equations are used to compute the complex transition amplitudes from Eq. (4) and transition probabilities $|C_m^\alpha(\rho, \infty)|^2$ for the charge exchange and direct scattering channels. It is necessary to explicitly consider a total of 14 product channels in order to obtain fully converged cross sections in the $O_2^+-O_2$ system at 8 eV center-of-mass kinetic energy. The competition between the various reaction channels is graphically displayed in Fig. 1 for the charge exchange channels where the relative transition probabilities are displayed as a function of impact parameter. The open area in the bottom portion of this figure represents the relative probability for the charge transfer channel forming slow $O_2^+(X^2\Pi_g, v'=1)$ ions and fast

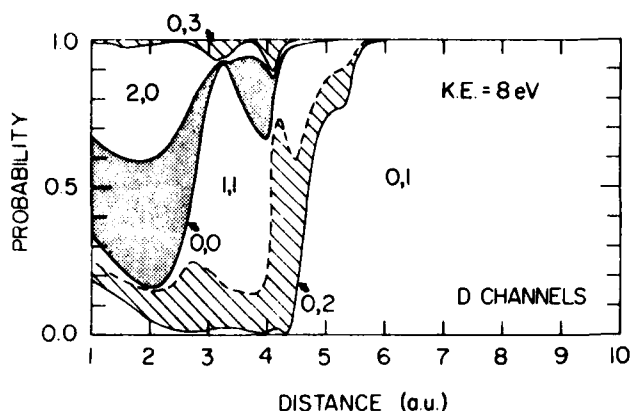


FIG. 2. Relative probabilities (eikonal method) for formation of specific product channels in 8.0 eV c.m. $O_2^+(X^2\Pi_g, v_g=1)$ + $O_2(X^3\Sigma_g^-, v_g'=0)$ direct, inelastic scattering collisions as a function of impact parameter distance in atomic units. The numbers associated with each area denote the vibrational quantum numbers of the respective $O_2^+(X^2\Pi_g, v')$ and $O_2(X^3\Sigma_g^-, v'')$ reaction products.

$O_2(X^3\Sigma_g^-, v''=0)$ molecules at different values of ρ for 8 eV collision energy. The cross-hatched area gives the relative probability for producing $O_2^+(X^2\Pi_g, v'=0)$ + $O_2(X^3\Sigma_g^-, v=1)$ products. The designations of the other various areas in this figure refer to product channels in which the ion and neutral vibrational levels are v' and v'' , respectively. For example, at R equal to 3.026 a.u., the relative probabilities for the $v', v''=1, 0$; $0, 1$; $0, 0$; $0, 2$; $1, 1$; $2, 0$; and $0, 3$ channels are 0.5963, 0.0303, 0.0047, 0.1249, 0.1534, 0.0868, and 0.0036, respectively. At large values of internuclear distance the resonant charge transfer channel predominates; however, at smaller values of ρ the inelastic charge transfer channels become important. Similar transition probabilities for the direct channels are displayed in Fig. 2. The notation in Fig. 2 is the same as in Fig. 1, where v' and v'' symbols denote the product ion and neutral vibrational levels, respectively. The elastic

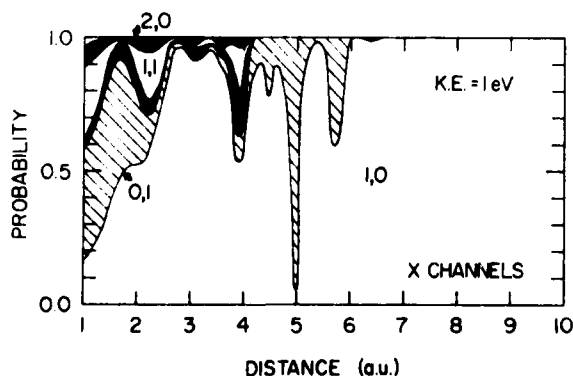


FIG. 3. Relative probabilities (eikonal method) for formation of specific product channels in 1.0 eV c.m. $O_2^+(X^2\Pi_g, v_g=1)$ + $O_2(X^3\Sigma_g^-, v_g'=0)$ charge exchanging collisions as a function of impact parameter distance in atomic units. The numbers associated with each area denote the vibrational quantum numbers of the respective $O_2^+(X^2\Pi_g, v')$ and $O_2(X^3\Sigma_g^-, v'')$ reaction products.

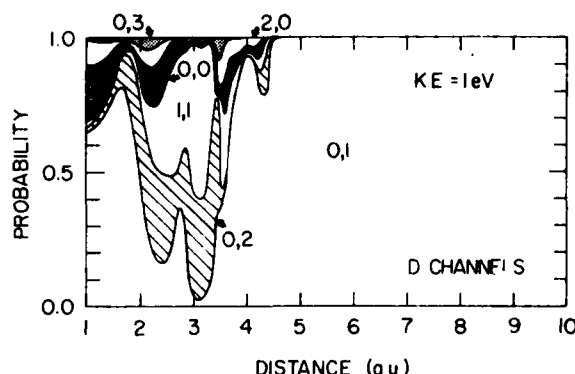


FIG. 4. Relative probabilities (eikonal method) for formation of specific product channels in 1.0 eV c.m. $O_2^+(X^2\Pi_g, v_g=1)$ + $O_2(X^3\Sigma_g^-, v_g'=0)$ direct, inelastic scattering collisions as a function of impact parameter distance in atomic units. The numbers associated with each area denote the vibrational quantum numbers of the respective $O_2^+(X^2\Pi_g, v')$ and $O_2(X^3\Sigma_g^-, v'')$ reaction products.

1,0 direct channel is not displayed but rather only the direct inelastic channels, which are the topics of this paper, are given in Fig. 2. At large values of R the 0,1 channel, corresponding to de-excitation of the ion, predominates. As R is reduced, the other inelastic channels become relatively more important.

The influence of lowering reactant ion kinetic energy on the relative transition probabilities is illustrated in Fig. 3. The relative contribution of the resonant 1,0 exchange channel is larger at 1 eV than at 8 eV, i.e., the inelastic processes generally become less important as the ion kinetic energy is lowered. At an impact parameter of 1.0 a.u. the different regions in Fig. 3, from top to bottom, represent the 0,3; 2,0; 1,1; 0,0; 0,1; and 1,0 channels, respectively. It is to be noted that the area corresponding to the 0,1 channel (vibrational de-excitation of the ion) is the dominant inelastic process at 1 eV. A similar situation occurs in the direct inelastic scattering channels shown in Fig. 4 with the 0,1 de-excitation channel playing a more important role at lower ion kinetic energies.

The relative contributions of the different reaction channels to the integral multistate charge transfer cross sections are illustrated in Fig. 5. Integral cross sections for individual inelastic channels have been obtained from Eq. (9) for a range of kinetic energies. Cross sections for channels having large energy defects tend to increase with ion kinetic energy, a fact consistent with the transition probabilities presented in the previous figures. Integral cross sections for the direct channels are presented in Fig. 6 for the same kinetic energy range. The magnitudes of the direct inelastic channels approximate those for the vibrationally inelastic charge transfer reactions. The direct channels with larger inelasticities begin to become important above several eV c.m. kinetic energy. Computation of accurate inelastic cross sections must take into account the curved trajectories as the reactant partners approach one another. The relative velocity range where the curved trajectories start to influence the inelastic pro-

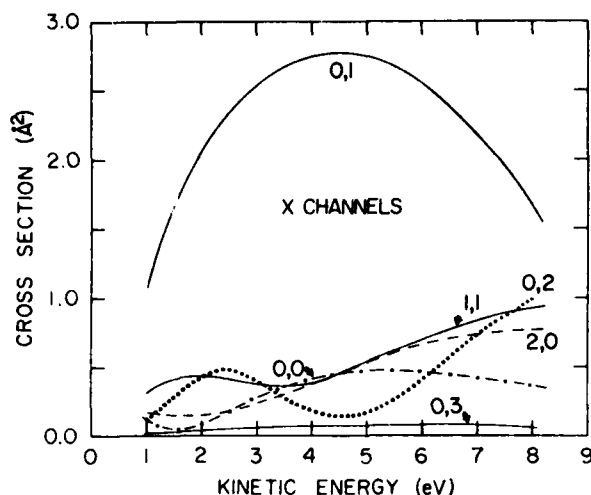


FIG. 5. Integral eikonal multistate cross sections (\AA^2) for excitation of specific product vibrational states in $\text{O}_2(X^2\Pi_g, v'_0=1) + \text{O}_2(X^3\Sigma_g^-, v''_0=0)$ charge exchange reactions. Cross sections for formation of specific ion and neutral product vibrational levels v' , v'' given as a function of c.m. kinetic energy.

cess will depend on the individual system and is examined in the following section.

Multichannel orbital treatment

The multistate orbital description of charge transfer uses Hamilton's equations to determine the actual relative trajectory $R(t)$ and the classical relative motion is evaluated using the "averaged" Hamiltonian

$$\bar{\mathcal{H}} \equiv \sum_{j=1}^3 \frac{p_j^2(t)}{2\mu} + \langle \Psi(r, t) | \mathcal{H} | \Psi(r, t) \rangle_r, \quad (10)$$

where the first term on the right-hand side represents

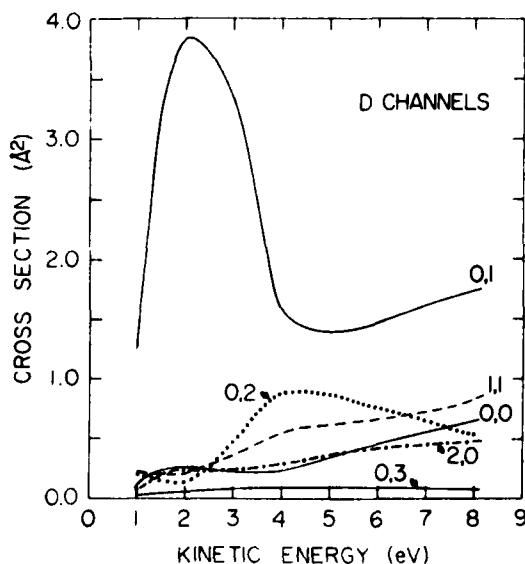


FIG. 6. Integral eikonal multistate cross sections (\AA^2) for excitation of specific product vibrational states in $\text{O}_2(X^2\Pi_g, v'_0=1) + \text{O}_2(X^3\Sigma_g^-, v''_0=0)$ direct, inelastic scattering reactions. Cross sections for formation of specific ion and neutral product vibrational levels v' , v'' are given as a function of c.m. kinetic energy.

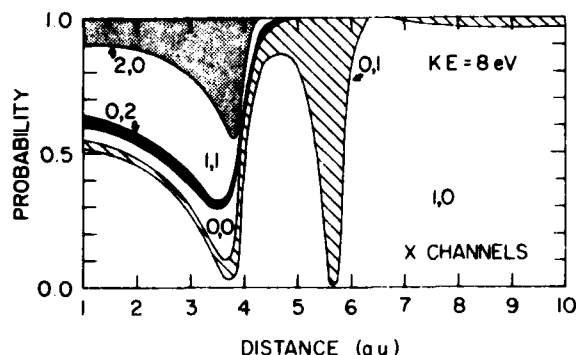


FIG. 7. Relative probabilities (orbital method) for formation of specific product channels in 8.0 eV c.m. $\text{O}_2(X^2\Pi_g, v'_0=1) + \text{O}_2(X^3\Sigma_g^-, v''_0=0)$ charge exchanging collisions as a function of impact parameter distance in atomic units. The numbers associated with each area denote the vibrational quantum numbers of the respective $\text{O}_2(X^2\Pi_g, v')$ and $\text{O}_2(X^3\Sigma_g^-, v'')$ reaction products.

the kinetic energy of relative motion. With the use of the wave function (2), the second term reduces to

$$\langle \Psi(r, t) | \mathcal{H} | \Psi(r, t) \rangle_r = \mathbf{S} [|a_m|^2 \epsilon_m + \mathbf{S} a_k^* a_m V_{km}(R) e^{i\epsilon_{km}t}] = V(R(t)), \quad (11)$$

which represents the averaged internal energy of the collision system. This term couples the response [Eq. (2)] of the collision partners to the relative motion via the expansion coefficients $a_n(t)$, analogous to $C_n(t)$, in Eq. (2) and Hamilton's equations become

$$\frac{\partial q_i}{\partial t} = \frac{p_i(t)}{\mu} \quad (12)$$

and

$$\frac{\partial p_i}{\partial t} = -\mathbf{S} \mathbf{S} a_k^*(t) a_n(t) \frac{\partial V_{kn}(R(t))}{\partial q_i} e^{i\epsilon_{kn}t}, \quad (13)$$

a set of six equations, in general, or four for scattering in a plane, which must be solved simultaneously with a coupled set (3). In order to relate the flux that flows through the incident area $\rho d\rho d\phi$ to the scattering solid angle $d\Omega$, $d\rho$ is given by

$$d\rho = (d\sigma/d\Omega)_{c1} d\Omega, \quad (14)$$

where $(d\sigma/d\Omega)_{c1}$ is the classical differential cross section for scattering by Eq. (11) and is just the Jacobian of the (ρ, Ω) transformation. The differential scattering cross section for the transition from state i to state f is computed from the equation

$$\sigma_{if}(\theta) = |a_f^s(t=\infty)|^2 (d\sigma/d\Omega)_{c1} d\Omega, \quad (15)$$

where a_f^s are the solutions of Eqs. (3) and (13), to be differentiated from C_f^s , the solutions of Eq. (3) with Eq. (5). If, however, more than one classical trajectory is scattered into solid angle $\Omega(\theta, \phi)$, then proper account of interference must be taken, including the phase of the contributing probability amplitude a_f^s . A full account of the procedure used here has already been given elsewhere¹⁶ in the full semiclassical treatment. The Burlish-Stoer method was used to evaluate the a_f^s from

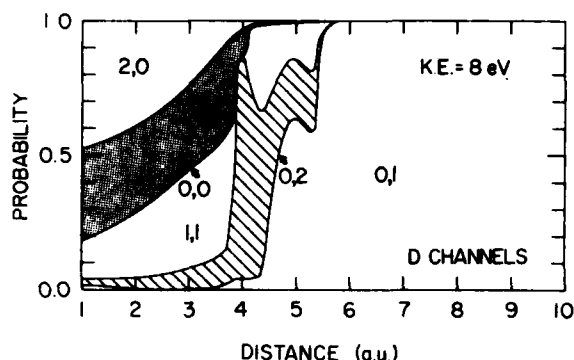


FIG. 8. Relative probabilities (orbital method) for formation of specific product channels in 8.0 eV c.m. $O_2(X^2\Pi_g, v_0=1) + O_2(X^3\Sigma_g^-, v_0'=0)$ direct, inelastic scattering collisions as a function of impact parameter distance in atomic units. The numbers associated with each area denote the vibrational quantum numbers of the respective $O_2(X^2\Pi_g, v')$ and $O_2(X^3\Sigma_g^-, v'')$ reaction products.

which integral cross sections have been obtained using the relation

$$Q_{fi}^a = 2\pi \int_0^\infty |a_f^a(\rho, t=\infty)|^2 \rho d\rho. \quad (16)$$

Relative transition probabilities $|a_f^a(\rho, \infty)|^2$ for the charge exchange channels are shown in Fig. 7 for the reactions of 8 eV $O_2(X^2\Pi_g, v=1)$ ions. The general features displayed in this figure are very similar to the multistate eikonal probabilities given in Fig. 1. This similarity is also reflected in the cross sections where the total multistate orbital charge transfer cross section, summed over all X channels, is 31.8 \AA^2 , which is

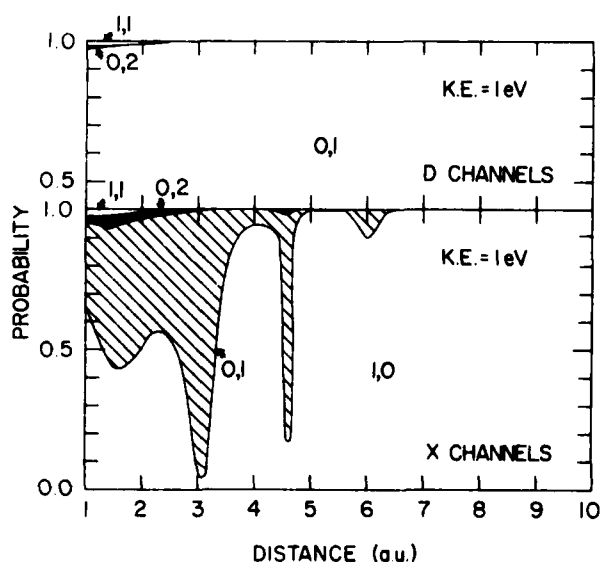


FIG. 9. Relative probabilities (orbital method) for formation of specific product channels in 1.0 eV c.m. $O_2(X^2\Pi_g, v_0=1) + O_2(X^3\Sigma_g^-, v_0'=0)$ direct, inelastic scattering collisions (D channels) and charge exchanging collisions (X channels) as a function of impact parameter distance in atomic units. The numbers associated with each area denote the vibrational quantum numbers of the respective $O_2(X^2\Pi_g, v')$ and $O_2(X^3\Sigma_g^-, v'')$ reaction products.

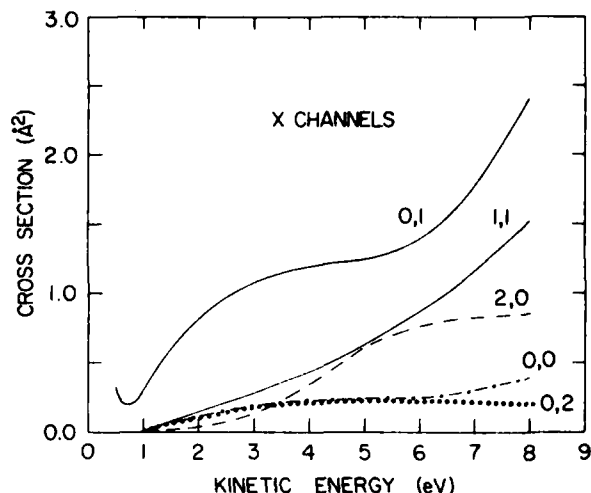


FIG. 10. Integral orbital multistate cross section (\AA^2) for excitation of specific product vibrational states in $O_2(X^2\Pi_g, v_0=1) + O_2(X^3\Sigma_g^-, v_0'=0)$ charge exchange reactions. Cross sections for formation of specific ion and neutral product vibrational levels v' , v'' are given as a function of c.m. kinetic energy.

close to the corresponding eikonal value of 33.6 \AA^2 . Relative transition probabilities for the 8 eV direct scattering channels in the orbital treatment are shown in Fig. 8. The overall behavior of these orbital probabilities for the D channels is similar to that for the eikonal approach (Fig. 2) but with some structural differences between the two at small values of R .

The differences between the transition probabilities in the two computational approaches are further emphasized in Fig. 9, where relative orbital transition probabilities at 1 eV are given for both the D and X channels. There is very little structure in the 1 eV orbital transition probabilities for the inelastic scattering

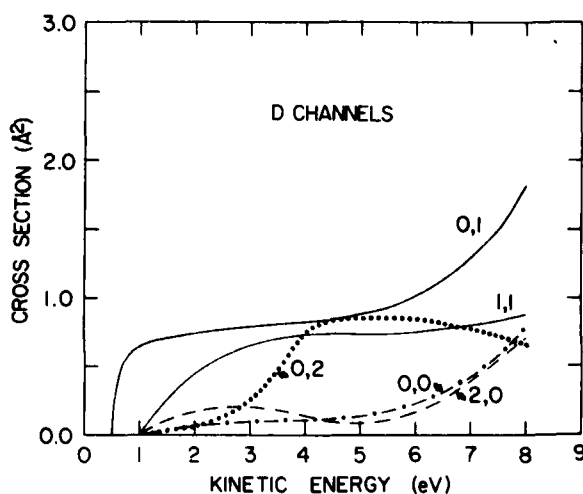


FIG. 11. Integral orbital multistate cross sections (\AA^2) for excitation of specific product vibrational states in $O_2(X^2\Pi_g, v_0=1) + O_2(X^3\Sigma_g^-, v_0'=0)$ direct, inelastic scattering reactions. Cross sections for formation of specific ion and neutral product vibrational levels v' , v'' are given as a function of c.m. kinetic energy.

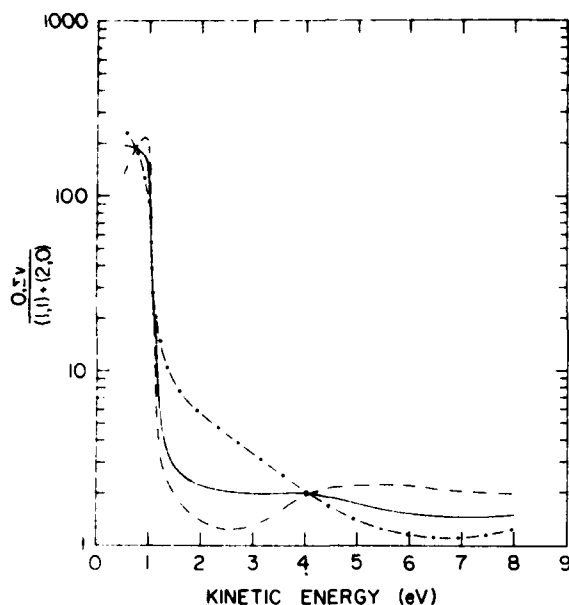


FIG. 12. Ratios of de-excitation ($0, \Sigma v$) to excitation $[(1,1) + (2,0)]$ cross sections for $O_2^+(X^2\Pi_g, v_0=1)$ ions as a function of c.m. kinetic energy in $O_2^+(X^2\Pi_g, v_0=1) + O_2(X^3\Sigma_g^-, v_0'=0)$ collisions. The dashed curve illustrates the ratio for the charge transfer channels X ; the dot-dashed curve gives the ratio for the direct scattering channels D ; the solid curve illustrates the ratio summed over the X and D channels. Calculations were performed using the orbital method.

processes with the $v', v'' = 0, 1$ channel dominating throughout the range of R , a fact in sharp contrast to data in Fig. 4. Likewise, the 1 eV orbital transition probabilities for charge exchange channels are relatively uncomplicated. The 1, 0 and 0, 1 channel transition probabilities are the largest at all impact parameters. The absence of contributions from reaction channels with larger energy defects in the orbital treatment is a result of the mutual scattering by the ion-molecule pair. The eikonal straight line approach artificially constrains the collision to be more "violent" at small values of R and thus overestimates the translational to vibrational energy conversion processes. This is reflected in the integral cross sections computed in the orbital treatment for the inelastic X and D channels which are given in Figs. 10 and 11. Although the cross sections for the inelastic channels are similar at 8 eV for the eikonal and orbital treatments, they diverge as the ion kinetic energy is lowered.

At ion kinetic energies below several eV, the inelastic processes in which the reactant $O_2^+(X^2\Pi_g, v_0=1)$ ion is deactivated, have the largest cross sections. The X channel with the largest cross section at 1 eV results in the formation of a slow ion in the $v=0$ level while the D channel with the largest cross section is one in which

the fast reactant ion ends up as a vibrationally deactivated product ion.

The resonant charge transfer channel involving reactant $O_2^+(X^2\Pi_g, v_0=1)$ ions has the largest cross section of any other channel. The ratio of the cross sections for resonant to inelastic channels increases as the reactant ion kinetic energy is lowered. The inelastic processes dominant at low ion kinetic energies are those that lead to vibrational de-excitation of the incident $v_0=1$ ion beam. Quantitative measure of the vibrational de-excitation of the ions is given in Fig. 12, where the cross section ratio (sum of all X and D channels with product ion $v'=0$)/(sum of the two largest X and D excitation channels) is presented. At low kinetic energies, the collisions that lead to vibrational de-excitation of the incident ion beam are approximately 200 times more probable than the vibrationally inelastic collisions. Thus, low velocity $O_2^+(X^2\Pi_g, v_0=1) - O_2(X^3\Sigma_g^-, v_0=0)$ collisions provide an effective means for quenching vibrational excitation in the incident ions.

ACKNOWLEDGMENT

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Appendix C

Ion-Ion Recombination as a Function of Ion and Gas Densities, Chem. Phys.

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ION-ION RECOMBINATION AS A FUNCTION OF ION AND GAS DENSITIES

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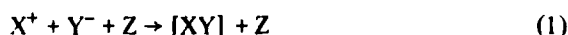
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We present a basic theory of the link between the low and high gas-density limits to ion-ion recombination under a general interaction V which now depends on the ion density and which is determined self-consistently with the recombination. Increase in ion density up to 10^{14} cm^{-3} causes little change to the recombination rates in direct contrast to that obtained in recent computer simulations.

Not only is the ion-ion recombination process \ddagger



of basic theoretical significance [1] in its own right, but it plays a key role in populating [2] the upper molecular electronic states of inert gas-halide lasers which operate not only at high densities N ($\approx \frac{1}{2}$ –10 atm) of the background gas Z but also at moderately high densities $N^\pm \approx 10^{12}$ – 10^{14} cm^{-3} of the positive and negative ions X^+ and Y^- . Reliable laboratory experiments are difficult and are as yet not forthcoming. All previous [3] theoretical treatments and experiments pertain tacitly to dilute ionization for which a coulombic ion-ion interaction is correct.

The purpose of this letter is to briefly outline a basic theory of the recombination rate α ($\text{cm}^3 \text{ s}^{-1}$) of (1) versus gas and ion densities, N and N^\pm , respectively and then to illustrate the key effects by appeal to a model version. In so doing, we will raise an interesting issue on the validity at all N of the ab initio adoption [4] of the Debye-Hückel interaction as a means of incorporating plasma sheathing effects when N^\pm is raised. Bates [5] has recently argued that this procedure is invalid at high N .

Recombination rate α . Let the negative ions of density $n^-(R, t)$ at time t stream across spheres of radius R each centered at each positive ion distributed N^\pm

\ddagger The square brackets denote that the product may not remain bound.

cm^{-3} . The time-dependent continuity equation is

$$\partial n^-(R, t) / \partial t - \nabla_R \cdot j = - \sum_{i=-V(R)}^C [\partial n_i^-(R, E_i, t) / \partial t]_S, \quad (2a)$$

where the net inward current (number of ions/s across unit area of an R sphere)

$$j = D[\nabla n^-(R, t) + n^-(R, t) \nabla(V/kT)] \\ \equiv -D e^{-V/kT} [d(n^- e^{V/kT}) / dR] \hat{R} \quad (2b)$$

arises from diffusional drift of the ions with relative diffusion coefficient D in the gas Z under an external field of potential $V(R)$. The collisional-sink term is

$$[\partial n_i^-(R, E_i, t) / \partial t]_S \\ = N \sum_{f=-V(R)}^{-M(R)} n_f^-(R, E_f, t) k_{fi}(R) \quad (3)$$

in terms of the phase-space densities $n_i^-(R, E_i, t)$ of R_i -ion pairs (i.e. ion pairs with internal energy E_i and fixed internal separation R) and of the collisional frequencies Nk_{fi} at which R_i -ion pairs are converted into R_f -ion pairs by collision with the gas bodies Z of density N (i.e. for $E_i \rightarrow E_f$ collisional transitions). The collisional sink is effective only when the lowest bound level $-V$ appropriate to fixed separation R lies at or

below the level $-S$ of energy E_{-S} below which the recombination is assumed to be stabilized against any upward collisional transitions, i.e. $-M$ is $\max[-V, -S]$.

Although expression (2a) has been derived [1] from the full Boltzmann equation which describes the evolution of the phase-space densities $n_i^-(R, E_i, t)$ by gas collisions, it can be written down immediately from macroscopic principles. The microscopic origin of the macroscopic current j of (2b) is the balance of *all* ineffective ion-neutral collisions in the absence of the sink, collisions which, in the presence of the sink, oversubscribe j by the amount (3) summed over all states i in (2a) between the lowest level $-V$ and the far continuum C . In a shell of radius R and thickness dR centered at each positive ion, distributed N^+ cm^{-3} , the number density $N^* dR$ of ion pairs is $4\pi R^2 dR N^+ n^-(R)$ which are assumed to decay explicitly with time as e^{-At} so that (2) becomes

$$\begin{aligned} & AN^+ \int_0^R 4\pi R^2 n^-(R) dR \\ & + 4\pi R^2 N^+ D \left[\frac{d}{dR} + \frac{d(V/kT)}{dR} \right] n^-(R) \\ & = \alpha_3(R) n^-(R) N^+, \end{aligned} \quad (4)$$

where the sink term (3) on integration over the volume of the R_E sphere has been replaced by

$$\begin{aligned} & \alpha_3(R) n^-(R) N^+ \\ & = N \int_0^R dR \left\{ \sum_{i=-E}^C \left[N_i^*(R, E_i) \sum_{f=-V}^{-E} k_{if}(R) \right. \right. \\ & \quad \left. \left. - \sum_{f=-M}^{-E} N_f^*(R, E_f) k_{fi}(R) \right] \right\}, \end{aligned} \quad (5)$$

the net balance between the rates of downflow and upflow of R -ion pairs past an arbitrary level $-E$ of negative energy. Although this replacement can be rigorously justified [1] it is physically correct and obvious.

Under thermodynamic equilibrium when the sink is neglected, the rhs of (5) vanishes. Since no effective collisional transitions occur at $R > R_E$, the outermost turning point associated with $-E$, the flux in the rhs of (4),

$$F_c(R) = \alpha_3(R) n^-(R) N^+ = \alpha N^+ N^-, \quad R \geq R_E, \quad (6)$$

is therefore constant for $R \geq R_E$. The lhs of (4) times $\exp(-At)$ then evolves with R to the complete time derivative of N^\pm with the result that the recombination coefficient appropriate to asymptotic ion density N^- is

$$\alpha = \alpha_3(R_E) n^-(R_E) / N^-, \quad (7)$$

which is determined by the rhs of (5) evaluated at R_E . Note from (7) that $\alpha_3 \exp(-V/kT)$ is the recombination rate α_{RCTN} that would pertain *provided* a Boltzmann distribution ($N^- e^{-V/kT}$) of ions were maintained, i.e. a reaction rate. Although α in principle, is determined in (5) by energy-change rates k_{if} and phase-space densities $n_i^-(R, E_i)$ of R_i -ion pairs, which, in turn, are solutions of a certain Boltzmann equation [1], a powerful approach based on prior or alternative knowledge of the "reaction rate" α_{RCTN} is as follows.

Neglect in (4) of the first term, which depends on $n^-(R)$ within R_E , implies,

$$\int_0^{R_E} 4\pi R^2 n^-(R) dR \ll 1, \quad (8)$$

since $A \approx \alpha N^-$, such that $N^- \ll (\frac{4}{3}\pi R_E^3)^{-1}$ and few ions are present in the recombination volume as measured by R_E . Then, integration of (4) under constant flux ($4\pi R^2 j N^+$) given by F_c of (6) yields,

$$\begin{aligned} n^-(R) &= N^- e^{-V/kT} [1 - (\alpha/\alpha_{\text{TRNS}}) P(R)/P(R_E)] \\ &= \frac{N^- e^{-V/kT} \alpha_{\text{TRNS}}(R)}{\alpha_{\text{RCTN}}(R) + \alpha_{\text{TRNS}}(R)}, \quad R \geq R_E, \end{aligned} \quad (9)$$

where the dimensionless quantity

$$P(R) = R_e \int_R^\infty R^{-2} e^{V/kT} dR, \quad R_e = e^2/kT, \quad (10)$$

in terms of the natural unit R_e of length, and where

$$\alpha_{\text{TRNS}}(R_E) = 4\pi K e / P(R_E) \equiv \alpha_H / P(R_E) \quad (11)$$

tends at high N to the correct Langevin-Harper rate [3,6] α_H for ions with relative mobility K in gas. Hence (7) yields

$$\begin{aligned} \alpha &= \alpha_{\text{RCNT}}(R_E) \alpha_{\text{TRNS}}(R_E) \\ & [\alpha_{\text{RCTW}}(R_E) + \alpha_{\text{TRNS}}(R_E)]^{-1} \end{aligned} \quad (12)$$

in terms of α_H which is known, and which $\approx N^{-1}$, and of the reaction rate α_{RCTN} and V , yet to be determined.

At low densities N , $\alpha/\alpha_{\text{TRNS}} \rightarrow 0$ as N^2 such that the ion density (9) is Boltzmann and α_{RCTN} may be uniquely identified with the low density limit to α . At low N , the reactivity of the ion pairs via three-body collisions with the gas is slow in comparison with the rate of ionic transport, so that this rate limiting step is characterized by α_{RCTN} . At high N , $\alpha/\alpha_{\text{TRNS}} \rightarrow 1$ such that $n^-(R)$ in (9) departs appreciably from Boltzmann for $R \approx R_E$. As N is increased the reactivity of the ion pairs via three-body collisions becomes so great compared with the rates of ionic transport that continued reaction at $R \approx R_E$ causes significant depletion in $n^-(R)$ over a localized region that $n^-(R)$ is far from Boltzmann. Hence the recombination process can be viewed as proceeding via ionic transport at rate α_{TRNS} followed by three-body reaction at rate α_{RCTN} such that the overall rate (12) is controlled by the rate limiting step.

The above theory establishes a firm theoretical foundation for (12) which, as noted previously by Bates and Flannery [6] is intrinsic to the expression of Natanson [7] and which is based on the equality of the transport and reaction fluxes.

Interaction V . As N^\pm is raised, the ion-ion interaction V can no longer be assumed ab initio to be purely coulombic but is given by appropriate solution of Poisson's equation

$$\nabla^2 V(R) = (4\pi e^2/\epsilon) [n^+(R) - n^-(R)], \quad (13)$$

when the local positive and negative ion densities are $n^\pm(R)$ and where ϵ is the dielectric constant of the gas Z . In the reference frame of the positive ion, $n^+(R)$ is the Boltzmann distribution $N^+ e^{V/kT}$ such that (13) for an R -symmetric distribution reduces with the aid of (9) to,

$$\frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial (V/kT)}{\partial R} \right) = (2R_S^2)^{-1} \{ e^{V/kT} - [1 - (\alpha/\alpha_{\text{TRNS}}) P(R)/P(R_E)] e^{-V/kT} \},$$

$$R \geq R_E, \quad (14)$$

where the "screening" distance is

$$R_S = (8\pi N^\pm R_e/\epsilon)^{-1/2}. \quad (15)$$

The $[]$ term, which depends on V , N and R in (14), tends to unity at low N for all R and increases at high N , from zero at $R \approx R_E$ to unity as $R \rightarrow \infty$. As $R_S \rightarrow \infty$, i.e. no plasma sheathing, the solution is coulombic so that an iterative solution valid for low N^\pm (large R_S) and high N in the vicinity of R_E is

$$V_H(R)/kT = -R_e/R + \frac{1}{12}(R/R_S)^2 \exp(-R_e/R_E),$$

$$R_E \lesssim R \ll R_S, \quad (16)$$

which is pure coulombic for $R \ll R_e$, or for $R^3 \ll 12R_e R_S^2$, i.e. when $N^\pm \lesssim 10^{14} \text{ cm}^{-3}$ at $R \lesssim R_e$. For low N , both exponential terms in the rhs of (14) are important. When $R \rightarrow \infty$, then $V \ll kT$ such that the solution to (14) can be obtained for all N linearizing the exponentials to give

$$V_L^{\text{DH}}(R) \rightarrow -(e^2/R) \exp(-R/R_S), \quad R \rightarrow \infty, \quad (17)$$

the Debye-Hückel interaction which can be used as a starting condition for the inward integration of (14) from large R .

Thus, the present method involves self-consistent solutions of α and V via (12) and (14). If an analytic form of the reaction rate α_{RCTN} which also depends on V is also unknown, then (14) is coupled to (5) in terms of the energy-change rates k_{if} , and of the phase-space densities $n_i^-(R, E_i)$, which are solutions of a certain Boltzmann equation [1] which also includes V .

Reaction-rate model. Rather than solve directly for $n_i^-(R, E_i)$ and hence for α from (5), assume that the sink term in (2a) can be replaced by a partially absorbing sphere of radius R_E such that (2a) is, in effect,

$$\frac{\partial n^-(R, t)}{\partial t} - \frac{1}{R^2} \frac{\partial (R^2 j)}{\partial R} = \Gamma_3 n^-(R) \delta(R - R_E), \quad (18)$$

where Γ_3 is the speed of reaction (via three-body collisions) for ions after being brought to R_E by ionic transport. In steady state, (18) incorporates the boundary condition,

$$j(R_E) = \Gamma_3 n^-(R_E), \quad (19)$$

which when multiplied by $4\pi R_E^2$ is equivalent to (7) such that

$$\alpha_3(R_E) = 4\pi R_E^2 \Gamma_3, \quad (20)$$

thereby confirming that the strength Γ_3 of the sink in (18) is the speed of reaction within R_E . The solutions

(9) and (12) follow directly from (18). For Γ_3 large compared with the speed of ionic transport, as at high N , the reactivity of the sink is effectively instantaneous and α tends to α_{TRANS} the transport rate, while low N implies Γ_3 small compared to the transport speed so that α tends to the reaction rate α_{RCTN} . It is worth pointing out that when (18), with its rhs set to zero, is solved subject to the boundary condition $n(R_E) = 0$, then the expression of Bates [8] is recovered, i.e. α is given entirely by α_{TRANS} . From (19) this zero-density boundary condition is equivalent to assigning an infinitely fast reaction speed Γ_3 to the sink, as is the case at high N . Thus (19), effectively allows for a finite reaction rate associated with a partially absorbing sink, rather than a fully absorbing sink implied by zero $n^-(R_E)$, equates the transport current at the boundary with the current of absorbed ions, and is valid for all N .

On recalling that each species of ion i have different mean free paths λ_i in the gas Z and different sink radii R_i , the model for the rate α_{RCTN} of reaction within R_E is therefore generalized from (20) to give

$$\alpha_{\text{RCTN}}(R_1, R_2) = \pi [R_1^2 W(X_1) C_1 E_1 + R_2^2 W(X_2) C_2 E_2 - R_S^2 W(Y_1) W(Y_2) G] \langle v_{12} \rangle, \quad (21a)$$

where $\langle v_{12} \rangle$ is some averaged ion-ion transport speed of approach, and where the probability for an ion i -neutral Z collision for ion pairs with internal separation $R \lesssim R_i$ increases with gas density to unity as [9]

$$W(X_i) = 1 - (1/2X_i^2)[1 - \exp(-2X_i)(1 + 2X_i)],$$

$$X_i = R_i/\lambda_i, \quad (21b)$$

for a straight-line trajectory. The factor

$$E_i = \exp[-V(R_i + \lambda_i)/kT] \quad (21c)$$

acknowledges the Boltzmann enhancement in the ion-number density due to the field at $R_i + \lambda_i$ at which the last ineffective ion-neutral collision occurs just before the ion enters the recombination sink within R_i . The factor

$$C_i = 1 + (2/3kT) \int_{R_i}^{R_i + \lambda_i} (\partial V/\partial R) dR \quad (21d)$$

acknowledges the focusing effect of the interaction on the assumed straight-line ion-ion trajectory between

$R_i + \lambda_i$ and R_i . The minimum of R_1 and R_2 is R_S such that $W(Y_1)W(Y_2)$ with $Y_i = R_S/\lambda_i$ is the probability of simultaneous ion-neutral collisions within R_S , a probability counted twice in the first two terms of (21a). Simple geometric arguments show that G in (21a) is either $C_1 E_1$ or $C_2 E_2$ depending on whether R_S is R_1 or R_2 , respectively.

The trapping radii R_i may now be deduced from kinematical considerations. The initial kinetic energy of relative motion of the positive ion 1 and negative ion 2 is

$$T_0 = \frac{3}{2}kT + \int_R^{R+\lambda} (\partial V/\partial R) dR, \quad (22)$$

since the ions on average are uninterrupted by collision only for separations between $R + \lambda$ and R . Ion pairs upon collision with a neutral become incapable of expanding outwards from R to $R + \lambda$ provided their final kinetic energy T_f is barely sufficient to provide the necessary energy required to increase R to $R + \lambda$ against the attractive force, i.e. when

$$T_f \leq \int_R^{R+\lambda} (\partial V/\partial R) dR. \quad (23)$$

Introduce a collision parameter δ to be fixed later such that the energy change $T_0 - T_f$ is δT_f . Thus the criteria (23) with (22) yields

$$V(R_E + \lambda) - V(R_E) = \frac{3}{2}kT/\delta, \quad (24)$$

to be solved for the trapping radii R_{Ei} corresponding to mean free paths λ_i where the subscript i is attached to quantities associated with each species of ion. In this strong-collision model, the interaction need only be specified at the trapping radii R_{Ei} . Solution of (24) for pure Coulomb field is

$$R_i = \frac{1}{2}\lambda_i [(1 + 4\delta_i R_T/\lambda_i)^{1/2} - 1] \\ \rightarrow \delta_i R_T \quad \text{as } N \rightarrow 0, \\ \rightarrow (\delta_i R_T \lambda_i)^{1/2} \quad \text{as } N \rightarrow \infty, \quad (25)$$

which decrease monotonically with λ_i and which satisfy $R_i(R_i + \lambda_i) = \delta_i \lambda_i R_T$, where the Thomson trapping radius R_T is $2e^2/3kT$.

At low N , $\lambda \rightarrow \infty$, and (24) sets $V_L(R_E)/kT$ equal to $-3/2\delta$ to be used directly in the rhs of Poisson's equa-

tion (14) which can now be solved to yield

$$V_L(R_E)/kT = -R_e/R_E + \frac{1}{12}(R_E/R_S)^2 B(\delta), \quad (26a)$$

where

$$B(\delta) = \exp(3/2\delta) - \exp(-3/2\delta). \quad (26b)$$

This potential which reduces to pure coulombic for $R \lesssim R_e$ and $N^\pm \lesssim 10^{14} \text{ cm}^{-3}$ is almost identical to (16) appropriate to high N . At low N , the trapping radii in (24) are therefore solutions of

$$B(\delta/18 R_S^2) R_{E0}^3 + R_{E0} = \delta R_T \quad (27)$$

and, for all N are given in terms of this solution R_{E0} by

$$R_E = \frac{1}{2}\lambda[(1 + 4R_{E0}/\lambda)^{1/2} - 1]$$

$$\rightarrow R_{E0}, \quad N \rightarrow 0,$$

$$\rightarrow (R_{E0}\lambda)^{1/2}, \quad N \rightarrow \infty, \quad (28)$$

in analogy with (25). Finally the low-density N limit to (21a) is

$$\alpha_{\text{TRNS}} \rightarrow \alpha_L = \alpha_{L1} + \alpha_{L2} = C_1 \delta_1^3 \alpha_{T1} + C_2 \delta_2^3 \alpha_{T2}, \quad (29a)$$

where C_i is $1 + \delta_i^{-1}$, and

$$\alpha_{Ti} = \frac{4}{3}\pi R_T^3 \langle v_{12} \rangle / \lambda_i \quad (29b)$$

is the Thomson partial recombination coefficient as $N \rightarrow 0$. The ratio \mathcal{R}_{Ti} of the exact low gas-density limit as given by the effectively exact microscopic theory of Bates and Flannery [10] to (29b) has been provided [11] over an extensive range of systems such that the collision parameter δ_i introduced above can now be uniquely obtained from solution of

$$\delta_i^3 + \delta_i^2 - \mathcal{R}_{Ti} = 0 \quad (30)$$

and α_{RCTN} tends, therefore, at low N to the exact quasi-equilibrium value [10].

Results of the present procedure, represented by (12) with α_{RCTN} given by (21) in terms of trapping radii (28), for the rate of



at 300 K are illustrated in fig. 1 as a function of gas density N for various ion densities N^\pm up to $\approx 10^{14} \text{ cm}^{-3}$, the validity limit of the present analysis. Results from the universal Monte Carlo plot procedure of Bates [12]

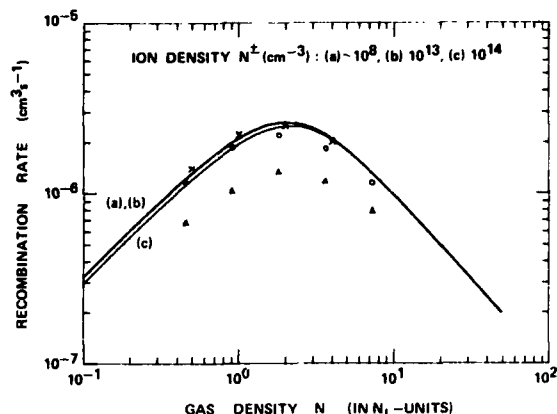


Fig. 1. Recombination rate coefficient α ($\text{cm}^3 \text{ s}^{-1}$) at 300 K for $(\text{Kr}^+ - \text{F}^-)$ in Ar, as a function of gas density N (in units of Loschmidt's number density $N_L = 2.69 \times 10^{19}$ at STP). —: present treatment with mobilities $K_1 = 2.16 \text{ cm}^2/\text{V s}$ and $K_2 = 3.29 \text{ cm}^2/\text{V s}$, for various ion densities N^\pm as indicated; \times : universal Monte Carlo (hard-sphere) plot [12]; \circ, Δ : Monte Carlo (polarization) results [4] at $N^\pm \approx 10^8$ and 10^{14} cm^{-3} , respectively.

for low N^\pm are also shown together with the direct Monte Carlo computer simulations of Morgan et al. [4] who adopted ab initio the Debye-Hückel interaction (17) for higher N^\pm . The general agreement between the various methods at low N^\pm can be considered excellent, but significant departure occurs at higher $N^\pm \approx 10^{14} \text{ cm}^{-3}$. The origin of the discrepancy at high N is due to the factor $P(R)$ in (11) which is much larger for the Debye-Hückel interaction (17) than for the interaction (16) predicted here, and, at low N , to the trapping radii given by (24) which for (17) are much smaller than those for (26) predicted here. The Debye-Hückel interaction (17) contains much stronger repulsion than either of (16) or (26). The theory outlined here predicts little departure of rates α up to $N^\pm \approx 10^{14} \text{ cm}^{-3}$. The theory indicates via (14) that the Debye-Hückel interaction is only valid at asymptotic R of little significance to the recombination. At high N , the ion distribution at R_E is far from Boltzmann equilibrium, and $V \gg kT$ such that linearization of even an equilibrium distribution is not valid at these R of significance to recombination.

In summary, therefore, we have provided here a timely theory of α as a function of gas and ion densities, have shown how the overall recombination may be viewed as proceeding via ion transport followed by

reaction such that the overall rate is determined by the rate-limiting step of transport/reaction, and have raised a timely, interesting and important question concerning validity of the *ab initio* assumption of the Debye-Hückel interaction in recombination studies. It will be of great interest to see whether improved Monte Carlo simulations which do not rely on this assumption will confirm the present theoretical predictions which are based on the (α, V) self-consistent solution of the interaction V in the presence of the recombination α . Finally, it is worth mentioning that transient "time-dependent" rates $\alpha(t)$ can be obtained [1] from (18) and these are important in medical radiology and in situations where intense ionization is deposited into or produced as a track within a localized system either by a high-energy beam of particles or radiation.

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Appendix D

Exact Closed Form Solution of the Generalized Debye-Smoluchowski Equation,

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**EXACT CLOSED-FORM SOLUTION OF THE GENERALIZED
DEBYE-SMOLUCHOWSKI EQUATION**

M. R. Flannery

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Exact Closed-Form Solution of the Generalized Debye-Smoluchowski Equation

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The first exact solution of the time-dependent Debye-Smoluchowski equation for diffusional drift under a general interaction in the presence of a reactive sink is presented. Associated time-dependent rates of chemical reactions in a dense gas are formulated and display the basic physical transition from reaction control to transport control as time progresses for a system initially in Boltzmann equilibrium.

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The number density $n^-(R, t)$ at time t of some species A (e.g., negative ions) drifting under interaction $V(R)$ across a sphere of radius R towards a central species B (positive ion) in a gas Z (or liquid) under the action of a reactive spherical sink of extent S from B is governed by the generalized Debye-Smoluchowski equation,

$$-\frac{dn^-(R, t)}{dt} = -\frac{\partial n^-(R, t)}{\partial t} + R^{-2} \frac{\partial}{\partial R} [R^2 j(R, t)] = \Gamma_3 n^-(R, t) \delta(R - S). \quad (1)$$

Here Γ_3 is the speed of reaction (via ion-pair-gas collisions) for ions after being brought to S

by the net inward diffusional-drift current,

$$j(R, t) = D \exp\left(\frac{-V}{kT}\right) \frac{\partial}{\partial R} \left[n(R, t) \exp\left(\frac{V}{kT}\right) \right], \quad (2)$$

in terms of the diffusion coefficient D ($\text{cm}^2 \text{s}^{-1}$) for relative diffusion of A and B in Z .

The number density N_i of all ion pairs AB with internal separation $R \neq S$ then decays at a rate,

$$\begin{aligned} -\frac{dN_i}{dt} &= -\frac{d}{dt} \int_S^\infty 4\pi R^2 N_i n^-(R, t) dR \\ &= -\frac{\partial N_i}{\partial t} + N_i^+ [F_\infty - 4\pi S^2 j(S - \epsilon, t)] \\ &= 4\pi S^2 \Gamma_3 n^-(S, t) N_i^+ = \alpha(t) N_i^+ N_i^-, \end{aligned} \quad (3)$$

where F_∞ is the rate (s^{-1}) of generation of negative ions at infinity, and where α is the time-dependent rate ($\text{cm}^3 \text{s}^{-1}$) of recombination appropriate to asymptotic ion densities N^\pm . If the ion current approaching S is absorbed by reaction within S , then $\lim_{\epsilon \rightarrow 0} j(S - \epsilon, t) = 0$. In steady state, the rate $4\pi R^2 j(R, t)$ from (1) is constant for $R \geq S + \epsilon$ and equals the production rate F_∞ in (3).

Equation (1) automatically incorporates the boundary condition

$$\Gamma_3 n^-(S, t) = \lim_{\epsilon \rightarrow 0} j(S + \epsilon, t) \quad (4)$$

which follows on integration of (1) between $S \pm \epsilon$ and which equates the transported and absorbed currents at the boundary. At asymptotic R the correct solution of (1) tends to the Boltzmann distribution.

$$n^-(R - \infty, t) = N^- \exp(-V/kT). \quad (5)$$

Equation (1) is of basic significance not only to ion-ion recombination in gases¹ and ionic solutions but also to chemical reactions in a dense medium, to coagulation of colloids, to medical radiology, to diffusion and field controlled reactions in metabolizing systems (as enzyme-substrate reactions in a cell²), and to diffusion across a membrane. While an exact time-dependent solution to (1) can be obtained² for the field-free ($V=0$) case, no exact solution has yet been determined for general V although a large body of literature exists on various approximate techniques³ for the Coulomb case. We provide here the first analytical exact solution of (1) for general $V(R)$, subject to the condition that $n^-(R, t=0)$ is prepared as the Boltzmann distribution (5).

The following exact solution is based on the novel transformation from R to the variable

$$\tilde{R} = \left\{ \int_R^\infty \exp[V(R)/kT] R^{-2} dR \right\}^{-1}; \quad (6)$$

$$d\tilde{R}/dR = (\tilde{R}/R)^2 \exp(V/kT),$$

which is not without its physical significance. It is related¹ to the probability that an R -ion pair will further contract by diffusion under V , in the presence of an instantaneous sink at S . Let,

$$n_v(R, t) = n^-(R, t) \exp(V/kT) \quad (7)$$

such that (1) with (6) reduces to

$$\frac{\partial n_v(\tilde{R}, t)}{\partial t} = \frac{\tilde{D}}{\tilde{R}^2} \frac{\partial}{\partial \tilde{R}} \left[\tilde{R}^2 \frac{\partial n_v(\tilde{R}, t)}{\partial \tilde{R}} \right] \quad (8)$$

subject to (4). The transformed diffusion coefficient

($\text{cm}^2 \text{s}^{-1}$) is

$$\tilde{D} = D \left(\frac{d\tilde{R}}{dR} \right)^2. \quad (9)$$

The form of this equation is, in the transformed \tilde{R} representation, identical with that for the field-free case in the original R representation. Accordingly, introduce scaled quantities,

$$\tilde{r} = (\tilde{R}/\tilde{S}) - 1, \quad \tilde{\tau} = \tilde{D}t/\tilde{S}^2, \quad n' = (\tilde{R}/\tilde{S})n_v(\tilde{R}, t) \quad (10)$$

such that (8) reduces to

$$\partial n'(\tilde{r}, \tilde{\tau}) / \partial \tilde{\tau} = \partial^2 n'(\tilde{r}, \tilde{\tau}) / \partial \tilde{r}^2. \quad (11)$$

This can be now solved by the method of Laplace transformation which automatically incorporates the initial condition. The full solution of (1) appropriate to spontaneous reaction [$\Gamma_3 \rightarrow \infty$ in (4)] is then, after some analysis,

$$n^{(s)}(R, t) = N^- \exp\left(-\frac{V}{kT}\right) \left[1 - \frac{\tilde{S}}{\tilde{R}} \operatorname{erfc} \left\{ \frac{(\tilde{R} - \tilde{S})}{2(\tilde{D}t)^{1/2}} \left(\frac{d\tilde{R}}{dR} \right) \right\} \right]. \quad (12)$$

The associated recombination rate is then

$$\alpha^{(s)}(t) = 4\pi S^2 j(S, t) / N^- = \alpha_{\text{TRNS}} \left[1 + \frac{S^2 \exp[-V(S)/kT]}{\tilde{S}(\pi \tilde{D}t)^{1/2}} \right] \quad (13)$$

which tends at long time $t \gg S^2/D$ to the steady-state transport rate

$$\alpha_{\text{TRNS}} = 4\pi S D = 4\pi D R_e / P(S), \quad (14)$$

where the natural unit of length R_e is (e^2/kT) and where

$$P(S) = R_e / \tilde{S} = R_e \int_S^\infty \exp(V/kT) R^{-2} dR. \quad (15)$$

Under condition of equilibrium with the field, the Einstein relation ($DR_e = Ke$) between D and the mobility K is valid. For a Coulombic attraction, the steady-state solution (14) is then

$$\alpha_{\text{TRNS}}^{(s)} = 4\pi Ke / [1 - \exp(-R_e/S)] \quad (16)$$

in accord with that of Bates.⁴

The boundary condition (4) for finite reaction, under a field is,

$$\Gamma_3(S) n^-(S, t) = D \exp\left[-\frac{V(S)}{kT}\right] \left\{ \frac{\partial}{\partial R} \left[n(R, t) \exp\left(-\frac{V}{kT}\right) \right] \right\}_S \quad (17)$$

which yields, in the transformed representation (6),

$$n_v(S, t) = \frac{\tilde{D}}{\tilde{\Gamma}_3(S)} \left(\frac{dn_v}{d\tilde{R}} \right)_S, \quad (18)$$

where the transformed speed of reaction is

$$\tilde{\Gamma}_3 = \Gamma_3(d\tilde{R}/dR). \quad (19)$$

Hence, the full time-dependent solution obtained from Laplace transformation of (11) subject to the initial Boltzmann distribution is, for a general interaction, given by

$$n^-(R, t) = N^- \exp(-V/kT) \left[1 + \left(\frac{\tilde{\alpha}}{\tilde{\alpha}_L} \right) \left(\frac{\tilde{S}}{\tilde{R}} \right) \{ \exp(2\tilde{\Omega} \tilde{\chi}) \exp \tilde{\chi}^2 \operatorname{erfc}(\tilde{\chi} + \tilde{\Omega}) - \operatorname{erfc} \tilde{\Omega} \} \right]. \quad (20a)$$

Here the associated quantities are defined as

$$\tilde{\chi}(t) = (1 + \tilde{\alpha}_3/\tilde{\alpha}_L)(\tilde{D}t)^{1/2}/\tilde{S}, \quad (20b)$$

$$\tilde{\Omega}(t) = (\tilde{R} - \tilde{S})/2(\tilde{D}t)^{1/2}, \quad (20c)$$

and

$$\tilde{\alpha} = \tilde{\alpha}_3 \tilde{\alpha}_L / (\tilde{\alpha}_3 + \tilde{\alpha}_L), \quad (20d)$$

in terms of the transformed reaction and transport rates,

$$\tilde{\alpha}_3 = 4\pi \tilde{S}^2 \tilde{\Gamma}, \quad \tilde{\alpha}_D = 4\pi \tilde{S} \tilde{D}. \quad (20e)$$

The ratio of these rates is, however, unchanged and given by

$$\frac{\tilde{\alpha}_3}{\tilde{\alpha}_L} = \frac{4\pi S^2 \Gamma_3 \exp[-V(S)/kT]}{\alpha_{\text{TRANS}}} = \frac{\alpha_{\text{RCTN}}}{\alpha_{\text{TRANS}}}. \quad (21)$$

Here α_{RCTN} denotes the reaction rate which from (3) is the recombination rate that would pertain provided a Boltzmann distribution of ions were maintained as at low gas densities when j in (2) vanishes. The full time-dependent recombination rate is now given by (20a) in (2) as

$$\alpha(t) = 4\pi S^2 \Gamma_3 n^-(S, t)/N^- = \alpha_\infty [1 + (\alpha_{\text{RCTN}}/\alpha_{\text{TRANS}}) \exp \tilde{\chi}^2 \operatorname{erfc} \tilde{\chi}], \quad (22a)$$

where $\tilde{\Omega}(R=S)$ in (20c) vanishes, $\tilde{\chi}$ in (20b) is, with the aid of (6), (9), and (21),

$$\tilde{\chi} = (1 + \alpha_{\text{RCTN}}/\alpha_{\text{TRANS}}) [(Dt)^{1/2}/S] \exp[V(S)/kT] [S \int_S^\infty \exp(V/kT) R^{-2} dR]^{-1}, \quad (22b)$$

and where

$$\alpha_\infty = \alpha_{\text{RCTN}} \alpha_{\text{TRANS}} / (\alpha_{\text{RCTN}} + \alpha_{\text{TRANS}}) \quad (22c)$$

is the steady-state rate of recombination which is controlled by the rate limiting step of reaction versus transport and which exhibits a form¹ characteristic of physical mechanisms in series. At high gas densities N , $\alpha_{\text{TRANS}} \ll \alpha_{\text{RCTN}}$ such that $\alpha_\infty \sim \alpha_{\text{TRANS}}$, the transport rate. At low N , $\alpha_{\text{TRANS}} \gg \alpha_{\text{RCTN}}$ such that $\alpha_\infty \sim \alpha_{\text{RCTN}}$. As t increases from zero, then

$$\exp \chi^2 \operatorname{erfc} \chi - 1 - \frac{2}{\sqrt{\pi}} \chi + \chi^2 - \frac{4}{3\sqrt{\pi}} \chi^3 + \dots \quad (23)$$

such that

$$\alpha(t=0) = \alpha_{\text{RCTN}} \left[1 - \frac{2}{\sqrt{\pi}} \left(\frac{\alpha_{\text{RCTN}}}{\alpha_{\text{TRANS}}} \right) \frac{(Dt)^{1/2}}{S} \exp[V(S)/kT] \left\{ S \int_S^\infty \exp(V/kT) R^{-2} dr \right\}^{-1} \right] \quad (24)$$

decreases initially from the reaction rate α_{RCTN} . As $t \rightarrow \infty$,

$$\exp \chi^2 \operatorname{erfc} \chi - \frac{1}{\chi \sqrt{\pi}} \left(1 - \frac{1}{2\chi^2} + \frac{3}{4\chi^4} \dots \right) \quad (25)$$

such that the long-time dependence is

$$\alpha(t \rightarrow \infty) = \alpha_\infty \left\{ 1 + \left(\frac{\alpha_\infty}{\alpha_{\text{TRANS}}} \right) \frac{S \exp[-V(S)/kT]}{(\pi Dt)^{1/2}} \left[S \int_S^\infty \exp(V/kT) R^{-2} dR \right] \right\} \quad (26)$$

which tends eventually to the steady-state rate α_∞ for $t \gg (S^2/D)$.

The ion density (20a) tends to the steady-state limit

$$n^-(R, t \rightarrow \infty) = N^- \exp(-V/kT) \left[1 - \left(\frac{\alpha_-}{\alpha_{\text{TRANS}}} \right) \frac{P(R)}{P(S)} \right] \quad (27)$$

which at low N is approximately Boltzmann but departs appreciably from Boltzmann at high N ($\alpha_- \sim \alpha_{\text{TRANS}}$) particularly in the region of the sink.

The full time dependence in (22a) for α is contained in (22b) for $\tilde{\chi}$ which, for a pure Coulomb attraction, varies as

$$\tilde{\chi}(\tau) = \left(1 + \frac{\alpha_{\text{RCTN}}}{\alpha_{\text{TRANS}}} \right)^{1/2} \tau^{1/2} \left(\frac{R_d}{S} \right)^{1/2} \left[\exp\left(\frac{R_d}{S}\right) - 1 \right]^{-1}, \quad (28)$$

where the scaled time is

$$\tau = t/(S^2/D) \quad (29)$$

in the units of (S^2/D) , the time approximately required for an ion to diffuse from the boundary to the center of the sink.

In Fig. 1 the time dependence is illustrated for the recombination rates $\alpha(t)$ resulting from (22) for various gas densities N (in units of N_L , the number density $2.69 \times 10^{19} \text{ cm}^{-3}$ at STP). The transport rate α_{TRANS} is given by (14) and the reaction rate α_{RCTN} for a fictitious (but representative) case of ions of equal mass (16 amu) and mobility $2 \text{ cm}^2/\text{V s}$ recombining in an equal mass gas at 300°K is obtained from a model^{1,2} which yields the exact quasiequilibrium rates³ at low N .

For high N , $\alpha(t)$ decreases initially from α_{RCTN} , which is $\gg \alpha_{\text{TRANS}}$, to its steady-state limit which is α_{TRANS} , i.e., for the assumed initial Boltzmann distribution, reaction first occurs spontaneously for the ions within S and then ion

transport is initiated in an attempt to compensate for the resulting hole in the distribution. For low $N \lesssim N_L$ ($\approx 1 \text{ atm}$), a linear variation of $\alpha(t)$ with t is exhibited since the reaction rate $\alpha_{\text{RCTN}} \ll \alpha_{\text{TRANS}}$ is always the rate limiting step. Thus the transition from reaction to transport is best observed for dense gases. Also shown in Fig. 1 are the characteristic time scales (S^2/D) for diffusion across a sink of radius S which is compressible with N . This effect could therefore be detected by modern laser spectroscopic techniques based on rotational or vibrational transitions in molecular ions. The steady-state rates are of course independent of the initial condition.

In summary, we have presented here the first exact closed-form analytical solution of the generalized Debye-Smoluchowski equation for diffusional drift in the presence of a reactive sink or source. The evolution of the rate of the overall process for an initial Boltzmann distribution exhibits the interesting phenomenon of control by reaction to control by transport, and illustrates the competition between these basic physical mechanisms as time progresses. This phenomenon is directly important to many areas as fluorescence quenching in solutions and in the disappearance rate of ionization tracks.

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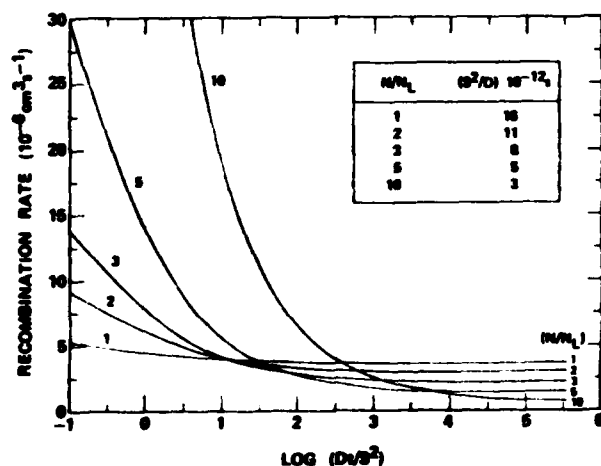


FIG. 1. Explicit time dependence of recombination rate $\alpha(t)$ at various gas densities, as indicated in units of Loschmidt's number N_L ($2.69 \times 10^{19} \text{ cm}^{-3}$ at STP). Characteristic times (S^2/D) for diffusion are also indicated.

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Appendix E

Ion-Ion Recombination in Dilute and Dense Plasmas, Int. J. Quant. Chem.:
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Ion-Ion Recombination in Dilute and Dense Plasmas

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Ion-Ion Recombination in Dilute and Dense Plasmas

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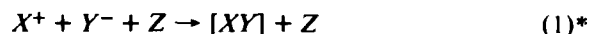
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Abstract

Theory of ion-ion recombination in a gas is provided as a function of gas density N , ion density N^\pm , and time. An approximate analytical solution to the generalized time-dependent Debye-Smoluchowski equation for reaction and diffusional drift under general ion-ion field is provided for an initial Boltzmann distribution of ions. The transition in the time-dependent rates $\alpha(t)$ of recombination from reaction to the rate limiting step of reaction and transport is illustrated for various N , together with the variation of the steady-state limit α with N . The method and results are of basic significance for situations ranging from medical radiological and biophysics to the rate of disappearance of ionization tracks.

1. Introduction

In this article we outline the first basic theory [1] of the recombination process



as a function of the density N of the gas Z , of the density N^\pm of the ions X^+ and Y^- and of the time t . The problem is fairly complex in that various macroscopic effects such as diffusion, mobility and the recombination sink must be initially addressed [1] in language of their microscopic collisional origin, so that various effects are not twice included (unwittingly) via some particular graft of macroscopic phenomena and microscopic principles. This detailed history has recently been established [1] via the Boltzmann equation and in this paper a simplified version which correctly blends microscopic and macroscopic effects is provided and the important results are illustrated. The work is significant also to chemical reactions in dense gases, to recombination in dilute ionic solutions and to the time rate of disappearance or diffusion of ionization tracks produced by a high-energy laser or beam of particles.

2. Recombination Rate

Let the negative ions of density $n^-(R,t)$ at time t stream across spheres of radius R each centered at each positive ion distributed $N^\pm \text{ cm}^{-3}$. The time-dependent continuity equation is

$$\frac{\partial n^-}{\partial t}(\mathbf{R},t) - \nabla_{\mathbf{R}} \cdot \mathbf{j} = - \sum_{i=-V(R)}^C \left[\frac{\partial n_i^-}{\partial t}(\mathbf{R},E_i,t) \right]_S \quad (2)$$

* The square brackets denote that the product may not remain bound.

where the net inward current (number of ions/s across unit area of an R sphere)

$$j = D[\nabla n^-(R,t) + n^-(R,t)\nabla(V/kT)] \\ \equiv -D \exp(-V/kT)(d/dR)[n^- \exp(V/kT)]\hat{\mathbf{R}} \quad (3)$$

arises from diffusional drift of the ions with relative diffusion coefficient D in the gas Z under an external field of potential $V(R)$. The collisional-sink term is

$$\left[\frac{\partial n_i^-}{\partial t}(R, E_i, t) \right]_S = N \sum_{f=-V(R)}^{-M(R)} n_f^-(R, E_f, t) k_{fi}(R) \quad (4)$$

in terms of the phase-space densities $n_i^-(R, E_i, t)$ of R_i ions (which form ion pairs with internal energy E_i and fixed internal separation R) and of the collisional frequencies Nk_{fi} at which an R_i ion pair is converted into an R_f ion pair by collision with the gas bodies Z of density N (i.e., for $E_i \rightarrow E_f$ collisional transitions). The collisional sink is effective only when the lowest bound level $-V$ appropriate to fixed separation R lies at or below the level $-S$ of energy E_S below which the recombination is assumed to be stabilized against any upward collisional transitions, i.e., $-M$ is $\max[-V, -S]$. Although expression (2) has been derived [1] from the full Boltzmann equation which describes the evolution of the phase-space densities $n_i^-(R, E_i, t)$ by gas collisions, it can be written immediately from macroscopic principles. The microscopic origin of the macroscopic current j of Eq. (3) is the balance of *all* ineffective ion-neutral collisions in the absence of the sink—collisions which, in the presence of the sink, over-subscribe j by the amount in Eq. (3) summed over all states i in Eq. (2) between the lowest level $-V$ and the far continuum C .

On integrating over the volume of each R sphere,

$$-N^+ \frac{\partial}{\partial t} \int_0^R [4\pi R^2 n^-(R, t) dR] + 4\pi R^2 N^+ j(R, t) \\ = \alpha_3(R) n^-(R, t) N^+ \quad (5)$$

where the sink term which effects recombination has been replaced by [1]

$$\alpha_3(R) n^-(R, t) N^+ = N \int_0^R dR \left[\sum_{i=-E}^C \left\{ N_i^*(R, E_i, t) \sum_{f=-V}^{-E} k_{if}(R) \right. \right. \\ \left. \left. - \sum_{f=-M}^{-E} N_f^*(R, E_f, t) k_{fi}(R) \right\} \right], \quad (6)$$

the net balance between the collisional rates of downflow and upflow of R ion pairs past some arbitrary bound level $-E$ of negative energy. In the shells of radii R and thickness dR , the number density of R_i ion pairs (or radial two-particle correlation function) is

$$N_i^*(R, E_i, t) = (4\pi R^2 dR) N^+ n^-(R, E_i, t) \quad (7)$$

We note for $R \geq R_E$, the outermost turning point associated with level $-E$, that

Eq. (6) tends to a constant since collisions with the gas atoms can be assumed impulsive [2] and change only the internal energy E_i of the ion pair and not their internal separation R . Hence, the flux $F_c(R)$ due to recombination,

$$F_c(R, t) = \alpha_3(R) n^-(R, t) N^+ = - \frac{dN^\pm}{dt} = \alpha N^+ N^-, \quad R \geq R_E \quad (8)$$

is therefore constant for $R \geq R_E$ and since the left-hand side of Eq. (5) evolves to the complete time derivative of the ion density, the overall recombination coefficient α in Eq. (7) appropriate to asymptotic ion density N^- is therefore,

$$\alpha(t) = \alpha_3(R_E) n^-(R_E, t) / N^- \quad (9)$$

which is determined by Eq. (6) from a knowledge of the phase space ion-pair densities N_i^* and the collisional rates $k_{ij}(R)$ for energy change.

By appeal to the Boltzmann equation for motion of an ion under an external electric field of intensity $\mathbf{E} \equiv (-\nabla V)$, the phase-space densities evolve in phase space and time as,

$$\begin{aligned} \frac{\partial n_i^-}{\partial t}(\mathbf{R}, \mathbf{v}_i, t) + \mathbf{v}_i \cdot [\nabla_{\mathbf{R}} n_i^-(\mathbf{R}, \mathbf{v}_i, t)] + \left(\frac{e\mathbf{E}}{m} \right) \cdot \nabla_{\mathbf{v}_i} n_i^-(\mathbf{R}, \mathbf{v}_i, t) \\ = \left(\frac{\partial n_i^-}{\partial t} \right)_{EL} - \left(\frac{\partial n_i^-}{\partial t} \right)_S \end{aligned} \quad (10)$$

where \mathbf{v}_i is the velocity of the negative ion at time t . Here the explicit time rate of change $(\partial n_i^- / \partial t)$ results from the following four mechanisms.

(1) The continuous transport (diffusion) of R_i ions across the R sphere is due to the \mathbf{R} -inhomogeneity in n_i .

(2) The continuous drift in velocity space due to \mathbf{E} produces an acceleration $(e\mathbf{E}/m)$ in each of the $n_i \Delta \mathbf{R}$ ions initially with velocity points \mathbf{v}_i within the phase element $\Delta \mathbf{v}_i \Delta \mathbf{R}$, i.e., the R_i ions drift in velocity space at the common rate $(e\mathbf{E}/m)$ and are therefore lost from the initial elementary region.

(3) The quasi-discontinuous change $(\partial n_i^- / \partial t)_{EL}$ of ions with velocities within $\Delta \mathbf{v}_i$ removes ions upon elastic ion-neutral collisions from one velocity element $\Delta \mathbf{v}_i$ to another. Replenishment to $\Delta \mathbf{v}_i$ is due to similar displacements from other elements of velocity space. Hence,

$$\begin{aligned} \left[\frac{\partial n_i^-}{\partial t}(\mathbf{v}_i, t) \right]_{EL} = \int_{\mathbf{v}_0} \left[\{ n_f^-(\mathbf{R}, \mathbf{v}_f, t) N_0(\mathbf{R}, \mathbf{v}_0, t) - n_i^-(\mathbf{R}, \mathbf{v}_i, t) N_0(\mathbf{R}, \mathbf{v}_0, t) \} \right. \\ \left. \int_{\Omega'} \{ g \sigma(g, \psi) d\Omega \} \right] d\mathbf{v}_0, \quad \mathbf{g} = (\mathbf{v}_i - \mathbf{v}_0) \end{aligned} \quad (11)$$

where $N_0(\mathbf{R}, \mathbf{v}_0, t)$ is the phase-space density of neutral gas species, and where the ion-neutral differential cross section at relative velocity $\mathbf{g} = (\mathbf{v}_i - \mathbf{v}_0)$ for elastic scattering by angle ψ into solid angle $d\Omega$ is $\sigma d\Omega$. The Ω integration is over that scattering region Ω' made accessible for the production of final ion and neutral velocities \mathbf{v}_f and \mathbf{v}_0 , respectively, consistent with initial fixed \mathbf{v}_i and \mathbf{v}_0 .

Note, however, that these elastic scattering terms produce energy changes (inelastic effects) in the internal energy E_i of an ion-pair system.

(4) The loss of ions $[\partial n_i^- / \partial t]_S$ due to the recombination sink tends to cause a redistribution in internal energies E_i of an ion pair with fixed internal separation R .

The elastic term in Eq. (11) produces *inelastic* transitions ($E_i \rightarrow E_f$) in an R_i ion pair and on integrating over $(1/4\pi)d\hat{v}_i$ an expression equivalent to Eq. (11) can therefore be written as,

$$\left[\frac{\partial n_i^-}{\partial t} (R, E_i, t) \right]_{EL} = N \left[\sum_{f=-\infty}^{\infty} n_f(R, E_f, t) k_{fi}(R) - n_i(R, E_i, t) \sum_{f=-\infty}^{\infty} k_{if}(R) \right] \quad (12)$$

where the internal energy E_i is $1/2 m v_i^2 + V(R)$.

Because of their continuous development in phase space, mechanisms (1) and (2) provide the "streaming" or transport terms. We note that the ion density N^\pm must be sufficiently low ($\lesssim 10^{16} \text{ cm}^{-3}$) compared with the gas density N_0 so that the effect of ion-ion direct collisions can be neglected in comparison with ion-neutral collisions which are only included in Eq. (11). Hence N_0 in Eq. (11) can be taken as the Maxwell-Boltzmann distribution such that Eq. (10) with Eqs. (11) and (4) is then the "linear" Boltzmann equation.

The recombination rate $\alpha(t)$ is therefore, in principle, determined as a general function of gas density N , ion density N^\pm , and time from Eqs. (9) and (6) via the time-dependent solutions of Eq. (10) for the phase-space densities. The interaction $V(R)$ between the ions can no longer be assumed *ab initio* to be pure Coulomb as N^\pm is raised. It is the appropriate solution of Poisson's equation

$$\nabla^2 V = \frac{4\pi e^2}{\epsilon} [n^+(R, t) - n^-(R, t)] \quad (13)$$

where the local positive and negative ion densities are

$$n^\pm(R, t) = 4\pi \int n_i^\pm(R, v_i, t) v_i^2 dv_i \quad (14)$$

and where ϵ is the dielectric constant of the gas Z . In the reference frame of the positive ion, $n^+(R, t)$ is simply the Boltzmann distribution

$$n^+(R, t) = N^+ \exp(V/kT) \quad (15)$$

Recombination is therefore fully determined by the solutions of Boltzmann's equation (10), Poisson's equation (13), and the kinetic equation (6) coupled together. Various theoretical procedures have been already proposed [1] for the solution of Boltzmann's equation (10) for the phase-space densities.

3. The Generalized Debye-Smoluchowski Equation: Transport and Reaction Rates

Rather than solve Boltzmann's equation (10) directly, assume that the sink term, Eq. (4) in Eq. (2), can be replaced by a partially absorbing sphere of radius $S(\equiv R_E)$, an assumption suggested by the constancy at $R \geq R_E$ of the microscopic kinetic expression (6) for the loss rate, such that Eq. (2) is in effect equivalent to the generalized Debye-Smoluchowski equation,

$$-\frac{\partial n^-}{\partial t}(R,t) + \frac{1}{R^2} \frac{\partial}{\partial R} [R^2 j(R,t)] = \Gamma_3 n^-(R,t) \delta(R-S) \quad (16)$$

where Γ_3 is the speed of reaction (via three-body collisions) for ions after being brought to S by the diffusional-drift current,

$$j(R,t) = D \exp(-V/kT) \frac{\partial}{\partial R} [n(R,t) \exp(V/kT)] \quad (17)$$

On integrating Eq. (16) over $4\pi R^2 dR$, then the continuous-source result is identical with Eq. (8) provided

$$j(S,t) = \Gamma_3 n^-(S,t) \quad (18)$$

such that

$$\alpha_3(S) = 4\pi S^2 \Gamma_3 \quad (19)$$

thereby confirming that the strength Γ_3 of the sink in Eq. (16) is the speed of reaction within S . As $\Gamma_3 \rightarrow \infty$, then

$$n^-(S,t) = 0 \quad (20)$$

for an instantaneous-reactive sink. Note that Eq. (16) is equivalent to the homogeneous equation (16) with its right-hand side set equal to zero solved subject to $\alpha_3(S)n^-(S,t)$ equal to $\alpha(t)N^-$.

Equation (16) is of basic significance not only to ion-ion recombination and chemical reactions in a dense medium but also to medical radiology, diffusion and field controlled reactions in metabolizing systems (as enzyme-substrate reactions in a cell [3], and diffusion across a membrane. While an exact time-dependent solution to Eq. (16) can be obtained [3] for the field-free ($V=0$) case, no exact solution has yet been determined for general V although a large body of literature exists on various approximate techniques [4] and numerical solutions [5] for the Coulomb case. We provide here an analytical solution of Eq. (16) for general $V(R)$, subject to the condition that $n^-(R,t=0)$ is initially prepared as the Boltzmann distribution, Eq. (15).

The following approximate solution is based on the novel transformation from R to the variable

$$R = \left\{ \int_R^\infty \exp[V(R)/kT] \frac{dR}{R^2} \right\}^{-1}; \quad \frac{d\tilde{R}}{dR} = \left(\frac{\tilde{R}}{R} \right)^2 \exp(V/kT) \quad (21)$$

a transformation novel without its physical significance. It is related [1] to the

probability P_e that an R_0 ion pair will further contract by diffusion under V , in the presence of an instantaneous sink at S (or else expand by diffusion expansion against V to infinite internal separation).

Let,

$$n_v(R, t) = n(R, t) \exp(V/kT) \quad (22)$$

such that Eq. (16) with Eq. (21) reduces to

$$\frac{\partial n_v(\tilde{R}, t)}{\partial t} = \frac{\tilde{D}}{\tilde{R}^2} \frac{\partial}{\partial \tilde{R}} \left[\tilde{R}^2 \frac{\partial n_v(\tilde{R}, t)}{\partial \tilde{R}} \right] \quad (23)$$

where the transformed diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$) is

$$\tilde{D} = D \left(\frac{d\tilde{R}}{dR} \right)^2 \quad (24)$$

The form of this equation is, in the transformed \tilde{R} representation, identical with that for the field-free case in the original R representation. Accordingly, introduce scaled quantities,

$$\tilde{r} = (\tilde{R}/\tilde{S}) - 1, \tilde{\tau} = \tilde{D}t/\tilde{S}^2, n' = (\tilde{R}/\tilde{S}) n_v(\tilde{R}, t) \quad (25)$$

such that Eq. (23) under assumption of constant \tilde{D} reduces to

$$\frac{\partial n'}{\partial \tilde{\tau}}(\tilde{r}, \tilde{\tau}) = \frac{\partial^2}{\partial \tilde{r}^2} n'(\tilde{r}, \tilde{\tau}) \quad (26)$$

which can be solved by the method of Laplace transformation which incorporates the initial condition.

The full solution of Eq. (16) appropriate to spontaneous reaction Eq. (20) is therefore, after some analysis,

$$n^{(S)}(R, t) = N^- \exp(-V/kT) \left\{ 1 - \frac{\tilde{S}}{\tilde{R}} \operatorname{erfc} \left[\frac{(\tilde{R} - \tilde{S})}{2\sqrt{\tilde{D}t}} \left(\frac{d\tilde{R}}{d\tilde{R}} \right) \right] \right\} \quad (27)$$

The recombination rate then reduces to

$$\alpha^{(S)}(t) = 4\pi S^2 j(S, t)/N^- = \alpha_{\text{TR}} \left\{ 1 + \frac{S^2 \exp[-V(S)/kT]}{\tilde{S}(\pi \tilde{D}t)^{1/2}} \right\} \quad (28)$$

where the steady-state transport rate

$$\alpha_{\text{TR}} = 4\pi \tilde{S} \tilde{D} = 4\pi D R_e / P(S) \quad (29)$$

with

$$P(S) = R_e / \tilde{S} = R_e \int_S^\infty \exp(V/kT) \frac{dR}{R^2} \quad (30)$$

in terms of R_e the natural length (e^2/kT). Under condition of equilibrium with the field when the Einstein relation written as ($DR_e = Ke$) holds, then for a Coulombic attraction, the steady-state solution is,

$$\alpha_{\text{TR}}^{(S)} = 4\pi Ke / [1 - \exp(-R_e/S)] \quad (31)$$

as previously obtained by Bates [6] in a steady-state analysis of an instantaneous sink.

The boundary condition Eq. (18) for finite reaction under a field is,

$$\Gamma(S)n^-(S,t) = D \exp[-V(S)/kT] \left\{ \frac{\partial}{\partial R} [n(R,t) \exp(V/kT)] \right\} \quad (32)$$

which yields, in the transformed representation of Eq. (21),

$$n_v(S,t) = \frac{\tilde{D}}{\tilde{\Gamma}(S)} \left(\frac{dn_v}{d\tilde{R}} \right)_S \quad (33)$$

where the transformed speed of reaction is

$$\tilde{\Gamma} = \Gamma(d\tilde{R}/dR) \quad (34)$$

Hence, after exercising due care, the full time-dependent solution obtained from the Laplace transformation of Eq. (26) subject to the initial Boltzmann distribution is given by, for a general interaction

$$n^-(R,t) = N^- \exp(-V/kT) \left[1 + \left(\frac{\tilde{\alpha}}{\tilde{\alpha}_D} \right) \left(\frac{\tilde{S}}{\tilde{R}} \right) \right. \\ \left. \times \{ \exp(2\tilde{\Omega}\tilde{\chi}) \exp\tilde{\chi}^2 \operatorname{erfc}(\tilde{\chi} + \tilde{\Omega}) - \operatorname{erfc}\tilde{\Omega} \} \right] \quad (35a)$$

where

$$\tilde{\chi}(t) = \left(1 + \frac{\tilde{\alpha}_3}{\tilde{\alpha}_D} \right) \frac{(\tilde{D}t)^{1/2}}{\tilde{S}} \equiv \left(1 + \frac{\tilde{\alpha}_3}{\tilde{\alpha}_D} \right)^{1/2} \left(\frac{Dt}{S^2} \right)^{1/2} \frac{\tilde{S}}{S} \exp V(S)/kT \quad (35b)$$

where,

$$\tilde{\Omega}(t) = (\tilde{R} - \tilde{S})/2(\tilde{D}t)^{1/2} \equiv (R - S)/2(Dt)^{1/2} \quad (35c)$$

since \tilde{D} is assumed constant in eq. (24) and where

$$\tilde{\alpha} = \frac{\tilde{\alpha}_3 \tilde{\alpha}_D}{\tilde{\alpha}_3 + \tilde{\alpha}_D} \quad (35d)$$

in terms of

$$\tilde{\alpha}_3 = 4\pi\tilde{S}^2\tilde{\Gamma}; \tilde{\alpha}_D = 4\pi\tilde{S}\tilde{D} \quad (35e)$$

The ratio of $\tilde{\alpha}_3$, the transformed reaction rate to $\tilde{\alpha}_D$, the transformed transport rate in Eq. (35) is therefore

$$\frac{\tilde{\alpha}_3}{\tilde{\alpha}_D} = \frac{\alpha_3 \exp[-V(S)/kT]}{\alpha_{TR}} = \frac{\alpha_{RN}}{\alpha_{TR}} \quad (36)$$

where α_{RN} is used to denote the recombination rate that would pertain provided a Boltzmann distribution of ions were maintained as at low gas densities, i.e.,

$$\alpha_{RN}(S) = 4\pi S^2 \Gamma_3 \exp[-V(S)/kT] \quad (37)$$

from Eqs. (19) and (36) such that Eq. (37) is the rate of reaction within S .

The full time-dependent recombination rate now follows from Eq. (35a) as,

$$\alpha(t) = \alpha_3 n^-(S, t) / N^- = \alpha \left[1 + \left(\frac{\alpha_{RN}}{\alpha_{TR}} \right) \exp \tilde{\chi}^2 \operatorname{erfc} \tilde{\chi} \right], \quad (38a)$$

where $\tilde{\Omega}(R = S)$ in Eq. (35c) vanishes, where $\tilde{\chi}$ in Eq. (35b) is, with the aid of Eqs. (21), (24) and (36),

$$\tilde{\chi} = \left(1 + \frac{\alpha_{RN}}{\alpha_{TR}} \right) \frac{(Dt)^{1/2}}{S} \exp[V(S)/kT] \times \left\{ S \int_S^\infty \exp(V/kT) R^{-2} dR \right\}^{-1} \quad (38b)$$

and where

$$\alpha = \frac{\alpha_{RN} \alpha_{TR}}{(\alpha_{RN} + \alpha_{TR})} \quad (38c)$$

is steady-state rate of recombination. Hence the radiation boundary condition (33) can be written as

$$n'(0, t) = (\alpha / \alpha_{RN}) \left(\frac{\partial n'}{\partial r} \right)_0$$

which incorporates the full absorption ($\alpha_{RN} \gg d$) and vanishing absorption ($\alpha \gg \alpha_{RN}$) conditions appropriate to diffusion-controlled and reaction-controlled processes respectively.

Thus the steady-state recombination rate α is controlled by the rate-limiting step of reaction versus transport. At high gas densities $N, \alpha_{TR} \ll \alpha_{RN}$ such that $\alpha \rightarrow \alpha_{TR}$ the transport rate. At low $N, \alpha_{TR} \gg \alpha_{RN}$ such that $\alpha \rightarrow \alpha_{RN}$.

As t increases from zero, then

$$\exp \chi^2 \operatorname{erfc} \chi \rightarrow 1 - \frac{2}{\sqrt{\pi}} \chi + \chi^2 - \frac{4}{3\sqrt{\pi}} \chi^3 + \dots \quad (39)$$

such that,

$$\alpha(t \rightarrow 0) = \alpha_{RN} \left[1 - \frac{2}{\sqrt{\pi}} \left(\frac{\alpha_{RN}}{\alpha_{TR}} \right) \frac{(Dt)^{1/2}}{S} \exp[V(S)/kT] \times \left\{ S \int_S^\infty \exp(V/kT) R^{-2} dr \right\}^{-1} \right] \quad (40)$$

decreases initially from the reaction rate α_{RN} . As $t \rightarrow \infty$, then

$$\exp \chi^2 \operatorname{erfc} \chi \rightarrow \frac{1}{\chi \sqrt{\pi}} \left(1 - \frac{1}{2\chi^2} + \frac{3}{4\chi^4} \dots \right) \quad (41)$$

such that the long-time dependence is

$$\alpha(t \rightarrow \infty) = \alpha \left\{ 1 + \left(\frac{\alpha}{\alpha_{TR}} \right) \frac{S \exp[-V(S)/kT]}{(\pi Dt)^{1/2}} \times \left[S \int_S^\infty \exp(V/kT) R^{-2} dR \right] \right\} \quad (42)$$

which tends eventually to the steady-state rate α for $t \gg (S^2/D)$.

The transient rates, Eqs. (40) and (42), for short and long intervals of time are best observed at high gas densities when $\alpha_{RN} \gg \alpha_{TR} \approx \alpha$, respectively. The full transient densities (35) and rates (37) are of basic significance to all diffusion-drift phenomena in gases or dilute solutions, as ion-ion, ion-atom, and atom-atom recombination in dense gases, or as coagulation of colloids in ionic solutions and in general to chemical reactions in dense gases.

The steady-state ion density from Eq. (33a) is

$$n^-(R, t \rightarrow \infty) = N^- \exp(-V/kT) \left[1 - \frac{\alpha}{\alpha_{TR}} \frac{P(R)}{P(S)} \right] \quad (43)$$

The full time dependence in Eq. (38a) for α is contained in Eq. (38b) for $\tilde{\chi}$ which, for a pure Coulomb attraction, varies as

$$\tilde{\chi}(\tau) = \left(1 + \frac{\alpha_{RN}}{\alpha_{TR}} \right) \tau^{1/2} \left(\frac{R_e}{S} \right) \left[\exp(R_e/S) - 1 \right]^{-1} \quad (44)$$

where the scaled time is

$$\tau = t/(S^2/D) \quad (45)$$

in units of (S^2/D) , the time approximately required for an ion to diffuse from the boundary to the center of the sink.

4. Simple Model for Reaction Rate

Assume that a reaction occurs following strong collisions between gas atoms and ion pairs with internal separations $R_i \leq R_i$. The trapping radii appropriate to interaction V is then the root of [7]

$$V(R_i + \lambda_i) - V(R_i) = \frac{3}{2} kT/\delta_i \quad (46)$$

where λ_i is the mean free path of the ion i ($i=1,2$) in the gas Z and where δ_i is a collision parameter so chosen that the deduced reaction rate reproduces in the limit of low N results [8] obtained from the quasiequilibrium microscopic treatment of ion-ion recombination at low N . Condition (46) originates from the requirement that an ion pair upon collision with Z is rendered incapable of expanding outwards from R_i to $R_i + \lambda$ where the next collision would occur. It is a generalization of Natanson's condition [9] and as $\lambda \rightarrow \infty$, Eq. (46) reduces to Thomson's criterion [10].

On recalling that each species of ion i have different mean free paths λ_i in the gas Z and different sink radii R_i , the model for the rate α_{RN} of reaction within R_E is therefore generalized from Eq. (37) to give [7]

$$\alpha_{RN}(R_1, R_2) = \pi [R_1^2 W(X_1) C_1 E_1 + R_2^2 W(X_2) C_2 E_2 - R_M^2 W(Y_1) W(Y_2) G] \langle v_{12} \rangle \quad (47a)$$

where $\langle v_{12} \rangle$ is some averaged ion-ion transport speed of approach, and where the probability for an ion i -neutral Z collision for ion pairs with internal separation $R \lesssim R_i$ increases with gas density to unity as

$$W(X_i) = 1 - (1/2 X_i^2) [1 - \exp(-2X_i)(1 + 2X_i)], \quad X_i = R_i/\lambda_i \quad (47b)$$

for a straight line trajectory. The factor

$$E_i = \exp[-V(R_i + \lambda_i)/kT] \equiv \exp[V(R)/kT] \exp(-3/2\delta_i) \quad (47c)$$

acknowledgments the Boltzmann enhancement in the ion number density due to the field at $(R_i + \lambda_i)$ at which the last ineffective ion-neutral collision occurs just before the ion enters the recombination sink within R_i . The factor

$$C_i = \left[1 + \left(\frac{2}{3kT} \right) \int_R^{R+\lambda} \left(\frac{\partial V}{\partial R} \right) dr \right] \equiv (1 + \delta_i^{-1}) \quad (47d)$$

acknowledges the focusing effect of the interaction on the assumed straight-line ion-ion trajectory between $(R_i + \lambda_i)$ and R_i . The minimum of R_1 and R_2 is R_M such that $W(Y_1)W(Y_2)$ with $Y_i = R_M/\lambda_i$ is the probability of simultaneous ion-neutral collisions within R_M , a probability counted twice in the first two terms of Eq. (47a). Simple geometric arguments show that G in Eq. (47a) is either $C_1 E_1$ or $C_2 E_2$ depending on whether R_M is R_1 or R_2 , respectively.

5. Interaction V

On inserting the steady-state ion density of Eq. (43) into Eq. (13), Poisson's equation become

$$\frac{1}{R^2} \frac{\partial}{\partial R} \left[R^2 \frac{\partial}{\partial R} (V/kT) \right] = \left(\frac{1}{2R_S^2} \right) \left[\exp(V/kT) - \left\{ 1 - \left(\frac{\alpha}{\alpha_{TR}} \right) \frac{P(R)}{P(R_E)} \right\} \exp(-V/kT) \right], \quad R \geq R_E \quad (48)$$

where the "screening" distance is

$$R_S = (8\pi N \pm R_e/\epsilon)^{-1/2} \quad (49)$$

and where R_E is the sink radius S of Sec. 3. An analogous time-dependent equation follows by inserting $n^-(R, t)$ of Eq. (35a) into Poisson's equation, Eq. (13).

Hence the $\{ \}$ term of Eq. (48) contains an explicit dependance on $V(R)$ via $P(R)$ of Eq. (30) and implicit and explicit dependances via α_{TR} of Eq. (29) and

α_{RN} of Eq. (47a) in Eq. (38c). The interaction must therefore be solved from Eq. (48) self-consistently with the recombination.

At low N , the $\frac{1}{2}$ term of Eq. (48) tends to unity at all R , while, at high N , it increases from zero, at $R \approx R_E$, to unity at asymptotic R . For no plasma sheathing ($R_S \rightarrow \infty$), the interaction V is Coulombic.

When $V \ll kT$, the exponentials in Eq. (48) may be linearized to yield the solution

$$V(R) = -\frac{e^2}{R} \left(1 - \frac{\alpha}{2\alpha_H} \right) \exp(-R/R_S) - \frac{(\alpha/\alpha_H)e^2}{2R} \quad (50)$$

where

$$\alpha_H = 4\pi D R_E = 4\pi K e \quad (51)$$

is the Langevin transport rate. Direct numerical integration of Eq. (48) which may be replaced by equivalent three coupled first-order differential equations shows that Eq. (50) remains a highly accurate solution for $R \gtrsim 0.1 R_E$. When $\alpha \ll \alpha_H$ as at vanishing N , Eq. (50) yields

$$V^{DH}(R) = -\frac{e^2}{R} \exp(-R/R_S) \quad (52)$$

the Debye-Hückel interaction (DH). The recent Monte-Carlo simulations [12] based on this interaction DH are therefore invalid [11, 13] for the range of gas densities N covered. The interaction of Eq. (52) is valid only in the limit of vanishing gas density, i.e., as $N \rightarrow 0$ when the rate α of recombination is vanishingly small compared to the rate of ion transport. When $\alpha \approx \alpha_H$ as at high gas densities N , Eq. (50) is Coulombic (C) at $R \approx R_E$ which is much smaller than $R_S \approx 1.5 R_E$ appropriate to $N^\pm \approx 10^{14} \text{ cm}^{-3}$, and Eq. (50) tends to the mean of C and DH at asymptotic R which is self-consistent with the choice $\alpha = \alpha_H$.

6. Transient and Steady-State Rates

In Figure 1 is illustrated the time-dependence of the recombination rates $\alpha(t)$ obtained from Eq. (38) for various gas densities N (in units of N_L , the number density $2.69 \times 10^{19} \text{ cm}^{-3}$ at STP). The transport rate α_{TR} is given by Eq. (31) and the reaction rate α_{RN} is obtained from Eq. (47) for a fictitious (but representative) case of ions of equal mass (16 amu) and mobility $2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ recombining in an equal mass gas (for which $\delta_i = 0.6$ [7]) at 300 K.

For high N , $\alpha(t)$ decreases initially from α_{RN} , which is $\gg \alpha_{TR}$, to its steady-state limit which is α_{TR} , i.e., for the assumed initial Boltzmann distribution, reaction first occurs for the ions within S and then ion transport begins in an attempt to compensate for the resulting hole in the distribution. For low $N \lesssim N_L$ ($\equiv 1 \text{ atm.}$), a linear variation of $\alpha(t)$ with t is exhibited since the reaction rate $\alpha_{RN} \ll \alpha_{TR}$. Thus the transition from reaction to transport is best observed for dense gases. Here the large reaction rates originate from the greatly enhanced

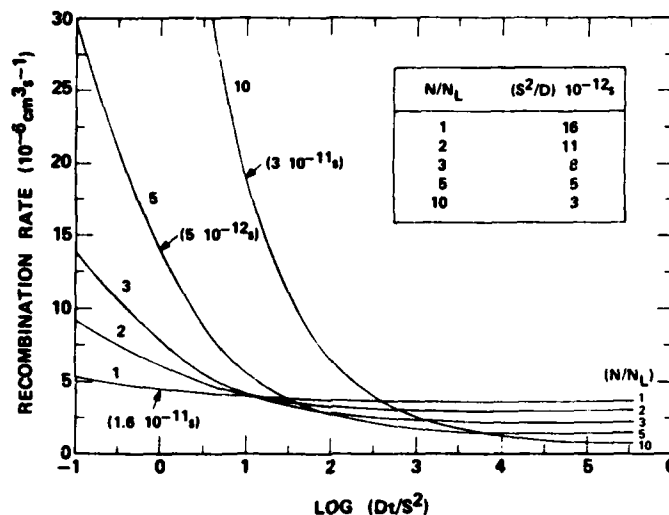


Figure 1. Explicit time dependence of recombination rate $\alpha(t)$ at various gas densities, as indicated in units of Loschmidt's number N_L ($2.69 \times 10^{19} \text{ cm}^{-3}$ at STP). Characteristic times (S^2/D) for diffusion are also indicated (from ref. 1).

Boltzmann factors E_i in Eq. (47a) which more than offsets the inherent reduction in the trapping radii R_i . Also shown in Figure 1 are the characteristic time scales (S^2/D) for diffusion across a sink of radius S which from Eq. (46) is compressible

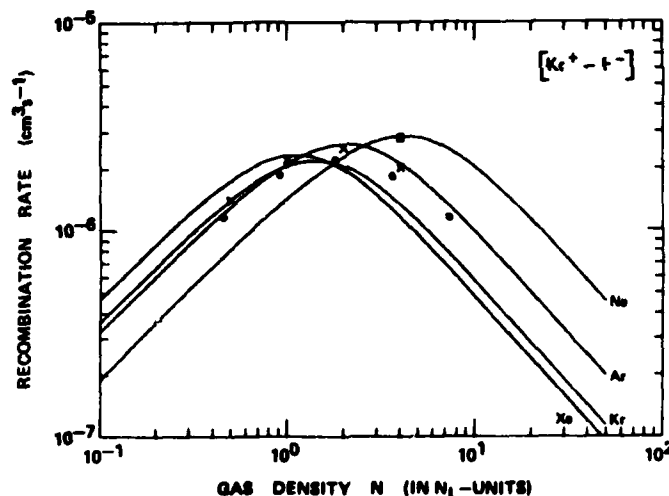
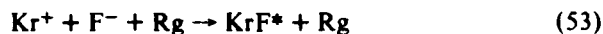


Figure 2. Recombination rate coefficient $\alpha(\text{cm}^3 \text{ s}^{-1})$ at 300 K for $(\text{Kr}^+ \text{ F}^-)$ in rare gases, as a function of gas density N (in units of Loschmidt's number density $N_L = 2.69 \times 10^{19}$ at STP): (—) Present treatment with experimental mobilities; (X, \square) universal Monte-Carlo (hard sphere) plot (ref. 14); (O) Monte-Carlo (polarization) results (ref. 12).

with N . This effect could therefore be detected by modern laser spectroscopic techniques based on rotational or vibrational transitions in molecular ions. The steady-state rates are independent of the initial condition.

In Figure 2 is illustrated the variation of the steady-state rates $\alpha(t \rightarrow \infty)$ for the realistic case



at 300 K with gas density N of various gases $\text{Rg} \equiv \text{Ne}, \text{Ar}, \text{Kr}, \text{Xe}$. Agreement with Monte-Carlo computer simulations [12, 14] is very good for low N^\pm . Figure 2 essentially shows the variation with N of the asymptotic limits of Figure 1.

Both figures therefore provide a comprehensive account of the recombination rate α as a function of time, and gas density. The present theory is also significant in other situations involving the rate of disappearance of a dense ionization track produced by a directed high energy beam of particles or radiation.

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Appendix F

Theory of Ion-Ion Recombination, Phil. Trans. Roy. Soc. (London) A 304,
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THEORY OF ION-ION RECOMBINATION

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A new and basic theory of ion-ion recombination as a function of gas density N is developed from basic microscopic principles. A key equation for the distribution in phase space of ion pairs is derived together with an expression for the resulting rate α

of recombination. Further development of the theory leads to interesting insights into the full variation with N of α , which is shown to yield the correct limits at low and high N . The recombination rate α is determined by the limiting step of the rate α_{rn} for ion reaction and of the rate α_{tr} for ion transport to the reaction zone. An analytical solution of the time-dependent Debye-Smoluchowski equation, which is a natural consequence of this theory, is provided for transport-reaction under a general interaction V , for an instantaneous reaction ($\alpha_{rn} \gg \alpha_{tr}$) and for a finite rate ($\alpha_{rn} \approx \alpha_{tr}$) of reaction within a kinetic sink rendered compressible by variation of gas density. Expressions for the transient recombination rates $\alpha(t)$ are then derived, and are illustrated. The exhibited time dependence lends itself to eventual experimental verification at high N .

A theory that investigates the variation of α with ion density N^\pm is also developed. Here the ion-ion interaction V can no longer be assumed *ab initio* to be pure coulomb but is solved self-consistently with the recombination. Recombination rates for various systems are illustrated as a function of N by a simplified method for the reaction rate. Finally, two theoretical procedures are proposed for the solution of the general phase-space ion distributions.

1. INTRODUCTION

Ever since the pioneering developments by Langevin (1903) of ion-ion recombination at high gas densities N , and by Thomson (1924) of the low density limit, theorists have sought a basic theory to link the linear three-body (Thomson) region to the nonlinear gas density region with the aim of eventual connection to the high density (Langevin) region in which the combined macroscopic effects of mobility (Langevin 1903) and of diffusion (Harper 1932, 1935) control events. Natanson (1959), by generalization of a method of Fuks (1958) on evaporation of water droplets in a gaseous medium, provided some insight to this link, although his approach remains phenomenological in the spirit of the approaches of both Langevin and Thomson. The concept of a trapping radius was invoked in all three studies and was so chosen by Thomson and Natanson that a single strong ion-neutral collision for ion pairs with separations within this radius produced recombination. Mechanisms resulting in mobility or diffusion, or both, were treated (if at all) as macroscopic.

These phenomenological approaches masked the essential theoretical problem, which is complex and difficult in that the macroscopic effects and recombination sinks require address in language of their basic microscopic origins. Any simplifications introduced through concepts of mobility, diffusion and trapping radii for description of macroscopic phenomena without recourse to their microscopic origin are inherently theoretically unsound, unless the full and detailed phase-space history of an ion pair has first been established, with all macroscopic characteristics being the effect of, rather than the cause of, such microscopic behaviour.

Suffice it to note this history has, in general, not been established, except in the low-density limit when diffusion-mobility effects are sufficiently fast to support equilibrium such that recombination is limited by reaction alone, as opposed to transport. Bates & Moffett (1966) and Bates & Flannery (1968) succeeded in developing the first rigorous theoretical account of recombination-reaction based on microscopic energy-change principles; they then established by quasi-equilibrium kinetics the essential development in internal energy E of ion pairs recombining solely by reaction. Bates & Mendaš (1978*a*), by distinguishing between expanding and contracting ion pairs, have proposed an interesting extension of the quasi-equilibrium method into the nonlinear region and have shown a variation of the recombination coefficient α with gas density N , consistent with the initial nonlinear ascent with N as given in the phenomenological

treatment of Thomson (1924). However, at pressures greater than 1 atm† (at 0 °C), the Thomson model predicts saturation in α , and fails. Coupling with the macroscopic effect of mobility, i.e. the diminishing effect of accelerations produced between collisions by the mutual ion-ion electrostatic field, is absent in both treatments. As will be shown here, the Thomson model is a model for the reaction rate and neglects the rate of ion transport, an assumption valid only at low N . Bates (1975) generalized the Harper-Langevin result by including (macroscopically) both diffusion and drift in the ion-transport rate which in the limit of high N is the rate of recombination since reaction proceeds infinitely fast.

The above references reflect the key pivotal theoretical developments, until now, that have contributed to the basic understanding of ion-ion recombination in a gas.

Since the overall theoretical problem is so complex and difficult, resort in the meantime has been made to procedures (Flannery 1978, Flannery & Yang 1978*a, b*, Wadehra & Bardsley 1978, Flannery 1976) that are all essentially modifications of Natanson's expression (based on the strong collision concept) or else to Monte-Carlo computer simulations (Bates 1980*a, b*; Bates & Mendaš 1978*b*, Bardsley & Wadehra 1980, Morgan *et al.* 1980) which, although they produce numerical coefficients α , do not deepen theoretical understanding of the basic issues involved. However, the Monte-Carlo results may exhibit special characteristics requiring further theoretical explanation (as in Bates 1980*c*). The renewed activity in recombination has been largely prompted by continuing interest in the overall problem, and in some measure by the key role (cf. Flannery 1979) of ion-ion recombination in populating the upper molecular states of rare gas-halide lasers which operate not only at high gas pressures ($\frac{1}{2}$ –10 atm) but also at high ion-densities $10^{12} \lesssim N^{\pm} \lesssim 10^{14} \text{ cm}^{-3}$. This is a region for which laboratory experiments of benchmark quality are as yet not forthcoming because of severe problems (even at low N^{\pm} , but especially at intermediate and high N).

The aim of this paper is to present the first basic theoretical account of a classical problem, i.e. the determination of the recombination rate α of



as a function both of gas density and of ion density. The first account of the explicit variation of $\alpha(t)$ with time will also be provided. To provide some insight, it is worthwhile to review the essential underlying phenomenological features of ion-ion recombination within a modern perspective.

1.1. Physical concepts

At high gas densities N , the relative velocity \boldsymbol{v} of the positive and negative ions X^+ and Y^- , labelled 1 and 2, respectively, is governed by \boldsymbol{v}_d , the drift velocity $(K_1 + K_2)\boldsymbol{E}$ acquired from the 1–2 mutual electrostatic field of intensity \boldsymbol{E} by the ions with mobilities $K_{1,2}$ in the neutral gas Z, labelled 3. The ion-neutral collision frequency (ν/λ_i) in terms of the mean free path λ_i of either ion i is very high and \boldsymbol{v}_d is therefore in equilibrium with the field. The constant steady-state \boldsymbol{v}_d is achieved as the balance between accelerations in the field direction *between* i –3 collisions, and decelerations *during* i –3 collisions. The net (inward) flux F_{in}^+ ($\text{cm}^{-3} \text{ s}^{-1}$) of negative ions crossing spheres of radii R_X centred at each positive ion, distributed with frequency $N^+ \text{ cm}^{-3}$, is about $4\pi R_X^2 \boldsymbol{v}_d N^+ N^-$ so that, under the assumption that all ion pairs with separations R less than R_X

† atm = 101325 Pa.

are assured of eventual recombination, the recombination rate at high gas densities N is equal to the rate of (drift) transport:

$$\alpha_h = -\frac{1}{N^+N^-} \frac{dN^\pm}{dt} = \frac{F_{in}^{+}}{N^+N^-} = 4\pi e(K_1 + K_2), \quad (1.2)$$

This is the Langevin result, which decreases as N^{-1} . The rate (1.2) is the rate α_{tr} of ionic transport in the absence of diffusion, which is appropriate only at asymptotic R , and is valid when the rate α_{rn} of reaction (by three-body collisions within R_X) is much faster than α_{tr} , as at high N where the large number of third bodies ensures instant deactivation of the ion pairs. The above method (fortuitously) provides the correct result only for a pure Coulomb attraction; for a general interaction, the full diffusional-drift equation (§ 2.4) must be solved.

At low gas densities N , ion-neutral collision frequencies are vanishingly small, so the relative 1-2 approach velocity v becomes much higher than the thermal velocity, and a large fraction of the close ion-ion 1, 2 encounters (within R_X) do not result in mutual neutralization by electron transfer. Of the velocity-changing i -3 collisions, the ones effective for recombination are those that occur for 1-2 separations $R \leq R_T$ where the electrostatic field is sufficiently strong for trapping. Since no angular momentum barrier at positive energies exists for pure coulomb attraction, trapping involves only those ion pairs with internal energy rendered negative by i -3 collisions. If it is assumed that recombination results from a single strong i -3 collision ($i = 1, 2$) within R_T centred at the other ion, then for low N , α increases linearly with N as

$$\alpha_{10} = K_{eq}(R_T) (\langle v \rangle / \lambda_1 + \langle v \rangle / \lambda_2) \equiv \frac{4}{3} \pi R_T^3 N \sigma_d \langle v \rangle, \quad (1.3)$$

in terms of some averaged collision frequency $\langle v \rangle / \lambda_i$ and of K_{eq} , the equilibrium constant ($\frac{4}{3} \pi R_T^3$) averaged over all energies for formation of R -ion pairs with internal separations $R \leq R_T$. The sum of the diffusion cross sections for each i -3 encounter is σ_d . For a suitable choice of the trapping radius R_T , (1.3) agrees with the low density limit of Thomson's result.

As N is raised, the ion-sink strength represented by α_{10} increases to such an extent that its effect on the number density $N_i(R)$ of R -ion pairs becomes important and must be coupled to the solution of N_i though the diffusion-drift equation thereby resulting in an overall increase with N less than linear (see § 2.3) and in eventual decrease, i.e. the rate of reaction increases, becomes comparable with, and eventually becomes much faster than the transport rate as N is increased. In contrast, however, Thomson assumed that as N is raised the probability $P_3(R_T/\lambda_i)$ of *effective*† ion-neutral collisions, for ion pairs with $R \leq R_T$, eventually increased to unity as

$$P_3(X) = W(X_1) + W(X_2) - W(X_1)W(X_2), \quad X_i = R_T/\lambda_i, \quad (1.4)$$

where the individual ion-neutral collision probability is (Loeb 1955)

$$W(X) = 1 - (1/2X^2) [1 - \exp(-2X)(1 + 2X)] \rightarrow \begin{cases} \frac{4}{3}X(1 - \frac{2}{3}X + \frac{2}{5}X^2 - \frac{1}{6}X^3 + \dots), & \text{low } N, \\ 1, & \text{high } N, \end{cases} \quad (1.5)$$

which yields (1.3) for N low, but which leads to a defective result at high N (although Thomson's survival-diffusion concept is essentially correct). The extension by Bates & Mendaš (1978a) into the nonlinear region is consistent with the initial nonlinear N -variation of (1.5). The Thomson rate is only the reaction rate, while Bates & Mendaš introduced the additional transport mechanism of diffusion.

The failure of the Thomson model at high N is due both to the neglect within R_T of the decreasing effect of accelerations produced by the ion-ion field between frequent ion-neutral

† In the sense of promoting the reaction phase of the recombination.

collisions, a mobility effect required for thermodynamic equilibrium in the absence of sources and sinks within R_T , and to the explicit neglect of ion transport by both diffusion and drift under V outside the reaction R_T -sphere. Both neglected effects, which originate with the transport of ions in phase space under a field, are a natural consequence of the basic theory (§2). Thus the Thomson rate is essentially the rate of reaction α_{rn} within an incompressible field-free sink S of ions brought to S not by ion transport (which is ignored) but by their thermal energy. Within the P_3 -factor of (1.4), diffusion is acknowledged only within the field-free sink through the decrease in survival rate of the ions towards increasingly effective collisions with an increasingly dense gas. The survival-collision probability P_3 remains therefore limited to unity at sufficiently high N (infinitely large collision probability for ions with infinitesimal survival probability).

It will subsequently become apparent that recombination occurs by reaction, at rate α_{rn} , of ion pairs (via three-body effective collisions) brought together by ion net transport at a rate α_{tr} such that the rate α of recombination is determined by the rate-limiting step, i.e. by

$$\alpha = \alpha_{rn} \alpha_{tr} / (\alpha_{rn} + \alpha_{tr}) \quad (1.6a)$$

$$\text{where} \quad \alpha_{rn} \sim (\pi R_T^2) P_3(X) \exp[-V(R_T)/kT] \langle v_{12} \rangle \quad (1.6b)$$

is the rate of reaction within R_T , and

$$\alpha_{tr} = 4\pi D \int_{R_T}^{\infty} \exp(KV/De) R^{-2} dR = 4\pi Ke [1 - \exp(-e^2/R_T kT)]^{-1} \quad (1.6c)$$

is the transport rate in terms of the coefficients $D \equiv K(kT/e)$ and K for relative diffusion and mobility respectively and of the integral which is related to the probability for diffusional escape in the presence of an instantaneous sink at R_T and an attractive interaction V which is taken as Coulomb. In this sense, Langevin and Thomson focused on each of the essential components (transport and reaction, respectively) required for a complete theory of recombination. Each component provides the correct limit: i.e. at high N when the reaction is instantaneous in comparison with transport ($\alpha_{rn} \gg \alpha_{tr}$), the overall rate α from (1.6a) reduces to (1.6c) while at low N , when the ionic transport is faster than the reaction ($\alpha_{tr} \gg \alpha_{rn}$), (1.6a) reduces to (1.6b).

The reaction rate α_{rn} is the recombination rate that would pertain (§2) provided a Boltzmann distribution of ions were maintained, a situation that results in no net diffusional drift.

Bates & Flannery (1969) have already noted that Natanson's expression, designed to cover all N , could essentially be written as (1.6a). By analogy with the behaviour of a steady current through an electrical network of two capacitances in series, Bates (1974) expressed a 'series' rate such as (1.6a) in terms of a theorem. It will subsequently become apparent that the full microscopic theory of ion-ion recombination places (1.6a) on a firm theoretical foundation and yields remarkable analogies to many macroscopic areas of physics (fluid dynamics, evaporation theory, coagulation of colloids, diffusion in a field, chemical reactions in dense gases, fluorescence quenching, electrostatics (cf. Appendix A), etc.) and that therein lies partly its fascination.

1.2. Physical concepts in the present theory

The present theory allows for the full evolution of the density of ion pairs in phase space by effective and ineffective† microscopic collisions, by inward and outward diffusion due respectively to the presence of the recombination sink (at small and intermediate R) and to the diffusional escape reaction to the effect of inward drift (at larger R), and by the accelerations

† In the sense that these collisions promote thermodynamic equilibrium by ion transport.

produced by mutual electrostatic ion-ion fields between ion-neutral collisions in an increasingly dense medium. In so doing, the macroscopic effects of diffusion and mobility are properly traced from their microscopic origins which in turn are responsible for the recombination sink, so that various physical mechanisms are not twice included (unwittingly) through some particular graft of macroscopic phenomena and microscopic mechanisms. In low density treatments (Bates & Moffett 1966, Bates & Flannery 1968), the acceleration due to the ion-ion interaction is included correctly; but as the gas density is raised, the diminishing effect of this acceleration due to increased collision frequencies must be properly acknowledged. Thermal equilibrium at high gas densities, without the effect of sinks, sources or chemical reactions, is achieved as a balance between the accelerations so produced by the field between collisions (or by macroscopic inward mobility) and the outward diffusion of ions due to the R -inhomogeneity produced by the ion-ion interaction. Presence of a sink naturally implies additional inward diffusion, which becomes effective at smaller and intermediate R .

1.3. Notation

The equation in the text in which the symbol is first precisely defined is given in parentheses.

α	recombination rate (cm^3s^{-1}), (2.51)
α_{rn}, α_{lo}	reaction rate (cm^3s^{-1}) or recombination rate appropriate to a Boltzmann distribution of ions, recombination rate at low gas densities, (2.61)
α_3	$\alpha_{rn} \exp[V(R)/kT]$, (2.44), such that $\alpha_3(R) n^-(R)$ is frequency of reaction within R -sphere.
α_h	Langevin rate ($4\pi Ke$), (1.2)
$\alpha_{tr}(R)$	transport rate $[\alpha_h \{R_e \int_R^\infty \exp(V/kT) R^{-2} dR\}^{-1}]$, (2.63)
α_{hi}	$\alpha_{tr}(R_E)$; recombination rate at high gas density, (2.63)
$\Gamma_3(R), \Gamma(R)$	speed of reaction of R -ion pairs, (2.82)
C	all states of ion pairs in the energy continuum, (2.5)
D	diffusion tensor, (2.37)
D	relative diffusion coefficient (cm^2s^{-1}) of positive and negative ions, (2.43)
D_S	diffusion coefficient in the presence of a sink, (5.49)
\mathcal{D}	diffusion drift operator, (2.46a)
δ	collision parameter, (4.15)
E	electric field intensity, (2.3)
$-E$	energy of arbitrary bound level ($-E$) of ion pair, (2.47a)
E_{-S}, E_{-V}, E_{-M}	energy of bound levels $-S$, $-V$, and $-M$ of ion pair such that $E_{-M} = \max[E_{-V}, E_{-S}]$, (2.49)
E_i	internal energy of the ion pair in state i
e	electronic charge ($4.80324 \times 10^{-10} \text{e.s.u.}$)
F	inward flux (negative ions s^{-1}) across a sphere centred at a positive ion, (2.69)
$F_0(v_1) dv_1$	Maxwellian distribution of speeds, (2.13)
g, g_1	ion-neutral relative speed, and velocity, (2.4)
$j(R, t)$	current (negative ions $\text{cm}^{-2}\text{s}^{-1}$) across an R -sphere centred at a positive ion, (2.45b)
k	Boltzmann constant ($1.38066 \times 10^{-23} \text{JK}^{-1}$)
K	relative mobility ($\text{cm}^2 \text{Stat V}^{-1} \text{s}^{-1}$) of positive and negative ions, (2.38), (2.43)

$k_{ii}(R)$,	collisional rate coefficient (cm^3s^{-1}) for conversion of R_i -ion pairs (with internal separation R and internal energy E_i) to R_i -ion pairs by collision with a third body (gas atom), (2.6)
$k_{ii}(E_i, E_i, R)$	
$L(v_i)$	peculiar path length of ions with speed v_i in absence of recombination sink, (5.34, 5.35)
$l_i(R, E_i)$	peculiar path length of ions in recombination process, (5.31)
λ_i	mean free path averaged over all speeds of ions in equilibrium, (1.3)
$-M$	bound level of energy E_{-M} such that $E_{-M} = \max[E_{-V}(R), E_{-S}]$, (2.11)
N	gas bulk density (cm^{-3}), (1.3)
N_L	gas density ($2.69 \times 10^{19} \text{cm}^{-3}$) at s.t.p. (Loschmidt's number), after (2.128)
N^\pm	ion bulk density (cm^{-3}), (1.2)
$N_0(\mathbf{R}, \mathbf{v}_0, t)$	phase-space gas density ($\text{cm}^{-3}/(\text{cm s}^{-1})^3$), i.e. gas density per unit $d\mathbf{v}_0$ -interval, (2.4)
$N(\mathbf{R}, t)$	configuration-space gas density (cm^{-3}) $\int N_0(\mathbf{R}, \mathbf{v}_0, t) d\mathbf{v}_0$, (2.34)
$n_i(\mathbf{R}, \mathbf{v}_i, t)$	phase-space density of negative ions, (2.2), (2.3)
$n_i(\mathbf{R}, v_i, t)$	$4\pi v_i^2 n_i(\mathbf{R}, \mathbf{v}_i, t)$ ($\text{cm}^{-3}/(\text{cm s}^{-1})$), density of negative ions per unit speed-interval about v_i , (2.8)
$n_i(\mathbf{R}, E_i, t)$	
$n_0(R, v_i)$	Maxwell-Boltzmann ion density per unit dv_i -interval, (2.13)
$n(\mathbf{R}, t)$	configuration-space negative ion density (cm^{-3}) $\int n_i(\mathbf{R}, \mathbf{v}_i, t) d\mathbf{v}_i$, (2.26)
$n(R, t)$	
$n^-(R, t)$	
$N_i^*(R, E_i, t)$	configuration density of R_i -ion pairs per unit dR -interval, $4\pi R^2 n(R, E_i, t) N^+$ (cm^{-4}) with internal energy $E_i < 0$, or per unit $dR dv_i$ -interval for $E_i > 0$, (2.10)
$N_i^*(R, E_i, \hat{\sigma}_i, t)$	phase-space density of R_i -ion pairs, i.e. configuration density per unit $d\mathbf{v}_i$ -interval, (2.2)
$N_0(R, E_i)$	Maxwell-Boltzmann ion pair density per unit $dR dE_i$ -interval, (2.14)
P_3	probability of an ion-pair-neutral collision, (1.4)
$P_0(R), P(R)$	$R_e \int_R^\infty \exp(V/kT) R^{-2} dR$, (2.56), which is such that $P(R_0)/P(R_E)$ is the probability that an R_0 -ion-pair contracts by diffusional drift in the presence of an instantaneous sink at R_E , (2.77)
$\mathcal{P}^c(R, R_E)$	(2.77a) for instantaneous sink and (2.77b) for finite-rate sink.
$\mathcal{P}^e(R, R_E)$	probability that an R -ion pair expands by diffusion to infinite internal separation against attractive force, (2.78)
$Q^{E, X}$	integral cross section for ion-neutral elastic (E) or charge-transfer (X) collisions, (2.7), Appendix B.
R_e	natural unit of length (e^2/kT or $e^2 K/De$) appropriate to coulomb attraction, (2.57) $\approx 55.7 \text{ nm}$ at 300 K.
$R_E, R(E)$	outermost turning point associated with bound-level of energy $-E$, (2.17), (2.51); maximum radius of three-body collision sink
R_i	Internal separation of ion pairs with internal energy E_i , before (2.3)
R_i	trapping radius appropriate to ion species i as a function of gas density, (4.17), (4.21)
R_s	screening length, (4.7)
R_T	Thomson trapping radius ($2e^2/3kT$) $\approx 37 \text{ nm}$ at 300 K, (4.17)
S	radius of strong-collision sink, compressible with increasing N , (2.70, 2.82)

$\sigma(g, \psi)$	differential cross section for ion-neutral scattering in the centre-of-mass frame
T	gas temperature (K)
τ_i	time-interval between collisions, (5.20), (5.34)
$V(R)$	ion-ion interaction potential
$-V$	bound level given by intersection of R and $V(R)$, (2.5)
$\mathbf{v}_0, \mathbf{v}_i$	velocities of gas atom and ion before collision, (2.4)
$\mathbf{v}'_0, \mathbf{v}'_i$	velocities of gas atom and ion after collision, (2.4)
W	probability for an ion-neutral collision, (1.5)
X_i	internal kinetic energy of relative motion of an ion pair, normalized to kT , (5.36)

2. THEORY OF ION-ION RECOMBINATION AS A FUNCTION OF NEUTRAL GAS DENSITY

In this section is presented the development of the basic equations to be solved for determination of the phase-space densities of ion pairs (§ 2.1), and the development (§ 2.2) of the basic expression for the rate α of recombination. An exact expression for the steady-state α is provided (§ 2.3) in terms of the rates for ionic transport and reaction, and similarities with a density-dependent reaction sink are explored in § 2.4. Finally, in § 2.5 is presented an analytical time-dependent solution of the Debye-Smoluchowski equation associated with a general spherical field for time-dependent ion densities and recombination rates $\alpha(t)$, a macroscopic equation which follows quite naturally from the present microscopic theory.

2.1. Basic equation for ion-pair phase density

Consider the drift of negative ions of density $n_i(\mathbf{R}, \mathbf{v}_i, t)$ and velocity \mathbf{v}_i at time t under interaction $V(R)$ across spheres of radius R centred on each positive ion, which are distributed with density $N^+ \text{ cm}^{-3}$, so that the number density $N_i^*(R, E_i, t)$ of ion pairs with reduced mass M_{12} , within the R -shells of thickness dR , with internal energy

$$E_i = \frac{1}{2} M_{12} v_i^2 + V(R), \quad (2.1)$$

and with internal motion directed along $\hat{\mathbf{v}}_i$, is

$$N_i^*(R, E_i, \hat{\mathbf{v}}_i, t) dR = 4\pi R^2 dR n_i(\mathbf{R}, \mathbf{v}_i, t) N^+. \quad (2.2)$$

Two approaches with similar effect can be adopted. The fate of an ion pair may be established by considering its previous history of *elastic and inelastic* collisions with the neutral gas. Here the mutual interaction $V(R)$ between the positive and negative ions is internal to the ion-pair system. The other approach, which we adopt here, is based on the motion of a given species of ion (negative ions, say) moving under a field of intensity $\mathbf{E} \equiv -\nabla V/e$ (which is conservative and now external to the negative ion) and undergoing *elastic* ion-neutral gas collisions. Expressions (2.1) and (2.2) link the basic quantities associated with each approach.

The present development is based on the Boltzmann equation (cf. Chapman & Cowling 1970), which (in this instance) equates the complete time rate of change of the phase-space distribution of ions with the appropriate ion-neutral collision rate integrated over the velocity distribution of the neutral gas species. The basic assumptions inherent in the derivation of the Boltzmann equation from the fully general Liouville equation (or from the B.B.G.K.Y.† hierarchy of

† After Bogoliubov, Born and Green, Kirkwood and Yvon who independently derived the equations between 1935 and 1949 (cf. Ferziger & Kaper 1972).

equations) for the phase-space distribution of all ionic and gas particles are (a) that only binary collisions occur via (b) interactions $V_1(R)$ of short range R outside which (c) the *precollision* velocities are distributed randomly with no correlation (molecular chaos), and (d) that the distribution functions do not vary appreciably during an encounter. These approximations are fully justified for percussive collisions between spherical particles. For van der Waals neutral-neutral and polarization ion-neutral attractions for which $V_1 \sim R^{-6}$, and $V_1 \sim R^{-4}$ respectively, long-range collisions do not, however, furnish the significant contribution to the collision integral, and so for ions moving in a gas, the Boltzmann equation remains valid.

The phase density $n_1(\mathbf{R}, \mathbf{v}_1, t)$ of negative ions (to be called R_1 -ions which form R_1 -ion pairs) of mass m ($\equiv M_{12}$ the reduced mass of an ion pair) in a conservative external field of intensity \mathbf{E} satisfies the Boltzmann equation (cf. Chapman & Cowling 1970, Ferziger & Kaper 1972, Holt & Haskell 1965)

$$\frac{\partial n_1(\mathbf{R}, \mathbf{v}_1, t)}{\partial t} + \mathbf{v}_1 \cdot [\nabla_{\mathbf{R}} n_1(\mathbf{R}, \mathbf{v}_1, t)] + \left(\frac{e\mathbf{E}}{m}\right) \cdot \nabla_{\mathbf{v}_1} n_1(\mathbf{R}, \mathbf{v}_1, t) = \left(\frac{\partial n_1}{\partial t}\right)_{\text{el}} - \left(\frac{\partial n_1}{\partial t}\right)_s, \quad (2.3)$$

in which the explicit time rate of change $(\partial n_1/\partial t)$ results from the following four mechanisms.

(a) The continuous transport (diffusion) of R_1 -ions across the R -sphere due to the \mathbf{R} -inhomogeneity in n_1 .

(b) The continuous drift in velocity space due to \mathbf{E} which produces an acceleration $e\mathbf{E}/m$ in each of the $n_1 \Delta \mathbf{R}$ ions initially with velocity points \mathbf{v}_1 within the phase element $\Delta \mathbf{v}_1 \Delta \mathbf{R}$, i.e. the R_1 -ions drift in velocity space at the common rate $e\mathbf{E}/m$ and are therefore lost from the initial elementary region.

(c) The quasidiscontinuous change $(\partial n_1/\partial t)_{\text{el}}$ of ions with velocities within $\Delta \mathbf{v}_1$ upon elastic ion-neutral collisions which therefore remove ions from one velocity element $\Delta \mathbf{v}_1$ to another. Replenishment to $\Delta \mathbf{v}_1$ is due to similar displacements from other elements of velocity space. Hence,

$$\left[\frac{\partial n_1(\mathbf{R}, \mathbf{v}_1, t)}{\partial t}\right]_{\text{el}} = \int_{\mathbf{v}_0} \int_{\Omega'} \{[n_1(\mathbf{R}, \mathbf{v}_1, t) N_0(\mathbf{R}, \mathbf{v}_0', t) - n_1(\mathbf{R}, \mathbf{v}_1, t) N_0(\mathbf{R}, \mathbf{v}_0, t)] [g\sigma(g, \psi) d\Omega]\} d\mathbf{v}_0, \quad (2.4)$$

where $N_0(\mathbf{R}, \mathbf{v}_0, t)$ is the phase-space density of neutral gas species, and where the ion-neutral differential cross section at relative velocity $\mathbf{g}_1 (= \mathbf{v}_1 - \mathbf{v}_0)$ for elastic scattering by angle ψ into solid angle $d\Omega$ is $\sigma d\Omega$. The Ω -integration is over that scattering region Ω' made accessible for the production of speeds associated with final ion and neutral velocities $\mathbf{v}_1(\mathbf{v}_1, \mathbf{v}_0, \Omega)$ and $\mathbf{v}_0'(\mathbf{v}_1, \mathbf{v}_0, \Omega)$, respectively consistent with initial fixed \mathbf{v}_1 and \mathbf{v}_0 . Note, however, that these elastic scattering terms produce energy changes (inelastic effects) to the internal energy E_1 of an ion-pair system.

(d) The loss of ions $(\partial n_1/\partial t)_s$ due to the recombination sink tends to cause a redistribution in internal energies E_1 of an ion pair with fixed internal separation \mathbf{R} and represents, in this sense, a transition probability. We seek to develop a theoretical expression for the microscopic and overall effect of this term.

Because of their continuous development in phase space, (a) and (b) provide the 'streaming' or transport terms. We note that the ion density N^\pm must be sufficiently low (less than about 10^{16} cm^{-3}) compared with the gas density N_0 so that the effect of ion-ion direct collisions can be neglected in comparison with ion-neutral collisions which are only included in (2.4). Hence N_0 in (2.4) can be taken as the Maxwell-Boltzmann distribution such that (2.3) with (2.4) is then the 'linear' Boltzmann equation.

As already mentioned, (2.4) produces *inelastic* transitions ($E_i \rightarrow E_f$) in an R_i -ion pair and on integrating over $v_i^2 d\mathbf{\hat{v}}_i$, an equivalent expression for (2.4) can, on replacing v_i by (2.1), therefore be written as,

$$\left[\frac{\partial n_i(R, E_i, t)}{\partial t} \right]_{el} = N \left[\sum_{f=-V}^C n_f(R, E_f, t) k_{fi}(R) - n_i(R, E_i, t) \sum_{f=-V}^C k_{if}(R) \right], \quad (2.5)$$

where N is the number density of gas atoms (or molecules) Z , and $Nk_{if}(R)$ is the frequency at which an R_i -ion pair is converted into an R_f -ion pair by *elastic* collision of either ion with Z , i.e.

$$N \sum_f^{t+\Delta t} k_{if}(R) \equiv Nk'_{if}(E_i, E_f, R) dE_f = \int_{v_{\min}}^{v_{\max}} 4\pi N_0(\mathbf{v}_0) \left[\int_{\Omega'} g\sigma(g, \psi) d(\cos \psi) d\phi \right] v_0^2 dv_0 \frac{1}{2} d(\cos \theta_i);$$

$$\cos \theta_i = \hat{\mathbf{v}}_0 \cdot \hat{\mathbf{v}}_i, \quad (2.6)$$

where v_{\min} , v_{\max} and Ω' are such that a final speed v_f of ion-ion relative motion is obtained from a given v_i and g and where Δt is the number of states in the energy interval dE_f about E_f . For example, for symmetrical resonance charge-transfer ion-neutral collisions, with cross section Q^x independent of relative collision speed, we have (Flannery 1980, Bates & Moffett 1966)

$$\sum_f k_{if}(E_i, E_f, R) \equiv \int k'_{if} dE_f = \left(\frac{1+c}{c} \right)^{\frac{1}{2}} \frac{Q^x}{2M_1 v_i} \int_{v_{\min}}^{v_{\max}} \frac{F_0(v_0) dv_0}{v_0} [v_0^2 - (v_i^2 + 2\Delta/M_1)]^{\frac{1}{2}}, \quad (2.7)$$

where F_0 is the Maxwellian distribution in speed v_0 of the neutral gas, c is the ratio of the mass M_i of the colliding ion to the mass of the spectator ion, and $\Delta = T_f - T_i$, the change in initial and final kinetic energies $\frac{1}{2}M_i(1+c)v_{i,f}^2$ of relative motion of the positive and negative ions. The f -summation, over all final bound and continuum states of the ion pair, can be replaced by an integral when a quasicontinuous spectrum of internal energies is assumed. Detailed expressions for the rates k_{if} associated with elastic ion-neutral collisions have been provided (Bates & Flannery 1968, Flannery 1981a). The sum or integration is taken over all final states f of the ion pairs, from the continuum C down to a level $-V$, the lowest accessible at R appropriate to interaction energy $V(R)$. Summation of (2.5), the elastic collision integral, over all initial levels E_i (or integration over all ion speeds v_i) is null, in accord with the fact that the number density of all ions is conserved in elastic collisions. Implicit in the rate (2.5) are the following assumptions.

(a) The gas is in thermal equilibrium so that its density distribution $N_0(\mathbf{v}_0)$ in gas velocities is isotropic, is independent of both time t and position \mathbf{R} and depends only on the speed v_0 .

(b) The number densities N^\pm of ions are much less than N_0 so momentum and energy imparted to the ions by their mutual field of intensity \mathbf{E} and transferred subsequently by collision with the gas Z have a completely negligible effect on $N_0(\mathbf{v}_0)$. When such thermal gradients do exist, they cause thermal diffusion in mixtures. The centre of mass of the ion pair is therefore assumed to be in thermodynamic equilibrium with the gas Z .

(c) There are spherical symmetric \mathbf{R} - and \mathbf{v} -distributions of negative ions about each central positive ion so that the ion densities in (2.4) and (2.5) are related at fixed R by

$$n_i(R, v_i, t) = 4\pi v_i^2 n_1(R, \mathbf{v}_i, t) \equiv n_1(R, E_i, t), \quad (2.8)$$

$$\sum_{f=-V}^C n_f(R, E_f, t) \equiv 4\pi \int_0^\infty n_1(R, \mathbf{v}_i, t) v_i^2 dv_i = \int_0^\infty n_1(R, v_i, t) dv_i. \quad (2.9)$$

Also the density N_i^* of ion pairs in the R -shell of thickness dR is related to the negative-ion density n_i by

$$N_i^*(R, v_i, t) dR = (4\pi R^2 dR) n_1(R, v_i, t) N^+ \equiv N_i^*(R, E_i, t) dR. \quad (2.10)$$

(d) The interaction V between the ions is switched off during the ion-neutral collision to be consistent with the left-hand side of (2.5), in which the field is *external* to each negative ion, i.e. the field cannot be included on both sides of the Boltzmann equation (2.3).

The sink term in (2.3) can be written as,

$$\left[\frac{\partial n_1(R, E_1, t)}{\partial t} \right]_S = N \sum_{t=-V(R)}^{-M(R)} n_t(R, E_t, t) k_{t1}(R) = \frac{N}{4\pi R^2 N^+} \sum_{t=-V(R)}^{-M(R)} N_t^*(R, E_t, t) k_{t1}(R) \quad (2.11)$$

where the energy of the bound level $-M$ is $E_{-M} = \max[E_{-V}(R), E_{-S}]$ in which E_{-S} is the negative energy of the bound level $-S$ below which recombination is assumed stabilized against any upward collisional transitions in energy. If the level $-V(R)$ of energy $E_{-V}(R)$ at R is above $-E_S$, then the sink term is ineffective. The sink term (2.11) in effect ensures that upward transitions, in internal energy, due to elastic ion-neutral collisions, from levels between $-V$ and $-M$ are not included in the right-hand side of the Boltzmann equation (2.3), and compensates for their oversubscription in (2.5). With the assumption of R -spherical symmetry in n_1 , (2.3), with the aid of (2.4)–(2.11), yields

$$\begin{aligned} \frac{\partial n_1(R, v_1, t)}{\partial t} + v_1 \left\{ \frac{\partial n_1(R, v_1, t)}{\partial R} - \frac{4\pi v_1^2}{mv_1} \frac{\partial}{\partial v_1} \left[\frac{n_1(R, v_1, t)}{4\pi v_1^2} \right] \left(\frac{\partial V}{\partial R} \right) \right\} \\ = \iint_{\Omega'} [n_t(R, v_t, t) N_0(\mathbf{v}_0') - n_1(R, v_1, t) N_0(\mathbf{v}_0)] [g\sigma(g, \psi) d\Omega] d\mathbf{v}_0 \\ \equiv N \left[\sum_{t=-M(R)}^C n_t(R, v_t, t) k_{t1}(R) - n_1(R, v_1, t) \sum_{t=-V(R)}^C k_{1t}(R) \right], \end{aligned} \quad (2.12)$$

as the basic equation for the solution of the phase-space densities of negative ions. The corresponding equation for phase-space densities $N_1^*(R, E_1, t)$ of ion pairs follows directly from (2.12) with the aid of (2.10) and of $\partial/\partial v_1 \equiv mv_1 \partial/\partial E_1$ at fixed R .

When thermodynamic equilibrium prevails, i.e. in the absence of the sink term (2.11), the steady-state solution to (2.12) is a product of two independent functions, one of position R and the other of speed v_1 and is such that both sides of (2.12) simultaneously vanish. The equilibrium number density of negative ions is found (after a not too trivial exercise) to be

$$n_0(R, v_1) dv_1 = N^- \exp[-V(R)/kT] F_0(v_1) dv_1 \quad (2.13a)$$

$$\equiv N^- \exp[-V(R)/kT] [4\pi v_1^2 (m/2\pi kT)^{3/2} \exp(-\frac{1}{2}mv_1^2/kT) dv_1], \quad (2.13b)$$

where $F_0(v_1) dv_1$ is the Maxwell distribution in ion speeds v_1 at temperature T . The equilibrium number density of R_1 -ion pairs in the R -shell of thickness dR and with internal energy in the interval dE_1 about E_1 is, therefore, with (2.1) and (2.2),

$$N_0(R, E_1) dR dE_1 = 4\pi R^2 dR \left[\frac{2}{\pi^{1/2}} \frac{1}{(kT)^{1/2}} [E_1 - V(R)]^{1/2} \exp(-E_1/kT) dE_1 \right] N^+ N^-, \quad (2.14)$$

of which one half move inward and one half move outward across the R -sphere, respectively. Also the rates k_{1t} satisfy the detailed balance relation (Flannery 1981a)

$$N_0(R, E_1) k_{1t}(R) = N_0(R, E_t) k_{t1}(R) \quad (2.15)$$

as expected. The equilibrium number density of all ion pairs in all permitted internal-energy states within the R -shell is

$$N_0(R) dR = dR \int_{E_1=-V(R)}^{\infty} N_0(R, E_1) dE_1 = 4\pi R^2 dR \exp[-V(R)/kT] N^+ N^-. \quad (2.16)$$

The equilibrium number density of ion pairs bound with negative energy in the interval dE about E is

$$N_0(E) dE = dE \int_0^{R_E(E)} N_0(R, E) dR = \frac{8\pi^{1/2}}{kT} [C(E) \exp(-E/kT) dE] N^+ N^-, \quad (2.17)$$

where $R_E(E)$ is the outermost turning point obtained from $E = V(R_E)$, and where for a pure coulomb attraction

$$C(E) = \int_0^{e^2/|E|} (e^2/R - |E|)^{1/2} R^2 dR = \frac{1}{3} \pi e^6 |E|^{-3/2}, \quad (2.18)$$

as obtained (Bates & Flannery 1968) for the equilibrium energy distribution of bound X^+-Y^- ion pairs in the absence of the gas Z .

The right-hand side of (2.12) can be replaced by $N_i^* \nu_i$ where ν_i is some averaged collision frequency. The characteristic time for substantial variation in the $\partial/\partial t$ -term in (2.12) is much longer than the mean time ν_i^{-1} between collisions so that the explicit time derivative in (2.12) is negligible with respect to the right-hand side. Hence, by setting

$$N_i^*(R, E_i, t) = N_i^*(R, E_i) \exp[-A(E_i) t], \quad (2.19)$$

in (2.12) and by ignoring the small decay frequency $A(E_i)$ of level i in comparison with ν_i , as in a steady-state solution, we have

$$\begin{aligned} \nu_i \left[\int_0^R 4\pi R^2 \frac{\partial}{\partial R} \left[\frac{N_i^*(R, v_i)}{4\pi R^2} \right] dR - \frac{4\pi v_i^2}{m v_i} \frac{\partial}{\partial v_i} \left\{ \frac{1}{4\pi v_i^2} \left[\int_0^R N_i^*(R, v_i) \frac{\partial V}{\partial R} dR \right] \right\} \right] \\ = \iint_{\Omega'} [N_i^*(R, v_i) N_0(\mathbf{v}_0') - N_i^*(R, v_i) N_0(\mathbf{v}_0)] (g \sigma d\Omega) d\mathbf{v}_0 \end{aligned} \quad (2.20a)$$

$$\equiv N \left[\int_0^R dR \sum_{t=-M(R)}^C N_i^*(R, E_t) k_{it}(R) - N_i^*(R, E_i) \sum_{t=-V(R)}^C k_{it}(R) \right] \quad (2.20b)$$

as the basic set of coupled integro-differential equations to be solved in general for the steady-state (R, E_i) -distributions of the ion-pair number densities $N_i^*(R, E_i)$. This set is solved subject to the boundary conditions that

$$N_i^*(R, v_i) = N_i^*(R, E_i) = \begin{cases} N_0(R, E_i), & E_i > 0, \quad R \rightarrow \infty, \\ N_0(R, E_i), & E_i \rightarrow \infty, \quad \text{all accessible } R, \\ 0, & E_i < -E_S, \quad R < R_c(E_S), \end{cases} \quad (2.21)$$

appropriate to the continuous generation of ion pairs with infinite separation.

Note that when the R -integration in (2.20) is taken over the full range of internal separations occupied by an ion pair of energy E_i , i.e. between the turning points R_c of $E_i = V(R)$, where $v_i(R_c, E_i)$ vanishes, then upon assuming that the left-hand side of (2.20) vanishes everywhere in this range we have

$$N_i^*(E_i) \sum_{t=-V}^C \langle k_{it} \rangle = \sum_{t=-S}^C N_i^*(E_i) \langle k_{it} \rangle \quad (2.22)$$

where $-V$ is the lowest bound energy level, the averaged rate is

$$\langle k_{it}(E_i, E_t) \rangle = \frac{1}{N_i^*(E_i)} \int_0^{R_M} N_i^*(R, E_i) k_{it}(E_i, E_t, R) dR, \quad R_M = \min[R(E_i), R(E_t)], \quad (2.23)$$

and the physical density of ion pairs with energy E_i is,

$$N_i^*(E_i) = \int_0^{R(E_i)} N_i^*(R, E_i) dR. \quad (2.24)$$

Results (2.22)–(2.24) apply when the left-hand side of (2.20) is assumed negligible at all R (rather than at the turning points alone), and correspond to the quasi-equilibrium result originally introduced by Bates & Moffett (1966) and by Bates & Flannery (1968) in their treatment of ion-ion recombination in the low gas-density limit, when the diffusional-drift streaming terms balance in a Maxwell-Boltzmann quasi-equilibrium. In general, however, the full set of basic equations (2.20) require solution subject to (2.21) as the gas density is increased.

2.2. Recombination coefficient α from derived equations of continuity, momentum and flux

To develop an expression for the recombination coefficient α in terms of ion-pair number densities $N_i^*(R, E_i)$, we proceed by constructing the appropriate flux or momentum equation from the Boltzmann equation (2.3) as follows. Returning again to (R, \mathbf{v}_i) -phase space occupied by the incoming negative ions of density $n_i(R, \mathbf{v}_i, t)$, we write the \mathbf{v}_i -averaged value of some physical quantity $P_i(R, \mathbf{v}_i, t)$ as

$$P(R, t) = \langle P_i \rangle = \frac{1}{n(R, t)} \int n_i(R, \mathbf{v}_i, t) P_i(R, \mathbf{v}_i, t) d\mathbf{v}_i, \quad (2.25)$$

where the configuration-space density is

$$n(R, t) = \int n_i(R, \mathbf{v}_i, t) d\mathbf{v}_i. \quad (2.26)$$

On multiplying the Boltzmann equation (2.3) by P_i and integrating over \mathbf{v}_i , we have

$$\begin{aligned} \frac{\partial n \langle P_i \rangle}{\partial t} - n \left\langle \frac{\partial P_i}{\partial t} \right\rangle + \nabla_R \cdot [n \langle P_i \mathbf{v}_i \rangle] - n \langle \mathbf{v}_i \cdot \nabla_R P_i \rangle - n \left(\frac{e\mathbf{E}}{m} \right) \cdot \langle \nabla_{\mathbf{v}_i} P_i \rangle \\ = \int_{\mathbf{v}_i} P_i(R, \mathbf{v}_i, t) \left(\frac{\partial n_i}{\partial t} \right)_{el} d\mathbf{v}_i - \int_{\mathbf{v}_i} P_i(R, \mathbf{v}_i, t) \left(\frac{\partial n_i}{\partial t} \right)_S d\mathbf{v}_i. \end{aligned} \quad (2.27)$$

However, microreversibility between the direct and corresponding reverse encounters applies and

$$\int_{\mathbf{v}_i} \int_{\mathbf{v}_0} \int_{\Omega} P_i n_i N_0 [g_i \sigma(g_i, \psi)] d\Omega d\mathbf{v}_i d\mathbf{v}_0 = \int_{\mathbf{v}_i} \int_{\mathbf{v}_0} \int_{\Omega} P_i n_i N_0 [g_i \sigma(g_i, \psi)] d\Omega d\mathbf{v}_i d\mathbf{v}_0, \quad (2.28)$$

since the collision is elastic ($g_i = g_i$), and since $d\mathbf{v}_i d\mathbf{v}_0 = d\mathbf{v}_i d\mathbf{v}_0$, so that, with the aid of (2.4),

$$\int_{\mathbf{v}_i} P_i \left(\frac{\partial n_i}{\partial t} \right)_{el} d\mathbf{v}_i = \int_{\mathbf{v}_i} \int_{\mathbf{v}_0} \int_{\Omega} [P_i(R, \mathbf{v}_i, t) - P_i(R, \mathbf{v}_i, t)] n_i N_0 [g \sigma(g, \psi)] d\Omega d\mathbf{v}_i d\mathbf{v}_0. \quad (2.29)$$

When P_i is set to unity the effect of elastic collisions is null (conservation of ions with all speeds) and (2.27) reduces to

$$\frac{\partial n(R, t)}{\partial t} + \nabla_R \cdot n(R, t) \langle \mathbf{v}_i \rangle = - \int_{\mathbf{v}_i} \left(\frac{\partial n_i}{\partial t} \right)_S d\mathbf{v}_i, \quad (2.30)$$

the equation of continuity in the presence of the sink S . When P_i is taken as the vector $m\mathbf{v}_i$, since $m(\mathbf{v}_i - \mathbf{v}_0) = \mu(\mathbf{g}_i - \mathbf{g}_0)$, where μ is the ion-neutral reduced mass, we can show, after some analysis, that

$$\int_{\mathbf{v}_i} m\mathbf{v}_i \left(\frac{\partial n_i}{\partial t} \right)_{el} d\mathbf{v}_i = - \mu \int \mathbf{g}_i R_D(g_i) n_i(R, \mathbf{v}_i, t) N_0(R, \mathbf{v}_0, t) d\mathbf{v}_i d\mathbf{v}_0, \quad (2.31)$$

where

$$R_D(g_i) = \int g_i (1 - \cos \psi) \sigma(g_i, \psi) d\Omega \quad (2.32)$$

is the momentum-transfer rate (cm^3s^{-1}) which, for an ion-neutral pure polarization attraction, is independent of g_1 , the relative speed $|(\mathbf{v}_1 - \mathbf{v}_0)|$. Since the gas is, on average, considered at rest (with respect to the centre of mass of the ion pair), $\langle \mathbf{v}_0 \rangle$ is zero such that

$$\int_{\mathbf{v}_1} \mathbf{v}_1 \left(\frac{\partial n_1}{\partial t} \right)_{\mathbf{e}_1} d\mathbf{v}_1 = -n(\mathbf{R}, t) \langle \mathbf{v}_1 \rangle \left[\frac{\mu}{m} R_D N(\mathbf{R}, t) \right] \equiv -n(\mathbf{R}, t) \langle \mathbf{v}_1 \rangle \nu, \quad (2.33)$$

where the configuration-space density of neutrals is

$$N(\mathbf{R}, t) = \int N_0(\mathbf{R}, \mathbf{v}_0, t) d\mathbf{v}_0, \quad (2.34)$$

and the term in square brackets, the frequency ν of ion-neutral collisions, is only approximately a constant for ion-neutral interactions that depart from the pure polarization form. This frequency can also be derived from (2.5) with the result that

$$n(\mathbf{R}, t) \langle \mathbf{v}_1 \rangle \nu = N \sum_{i=-\infty}^{\infty} v_i \sum_{j=-\infty}^{\infty} [n_i(\mathbf{R}, E_i, t) k_{i1}(\mathbf{R}) - n_1(\mathbf{R}, E_i, t) k_{1i}(\mathbf{R})], \quad (2.35)$$

where v_i can be expressed in terms of E_i by (2.1). Hence with (2.33), (2.27) yields the momentum equation

$$\frac{\partial [n(\mathbf{R}, t) \langle \mathbf{v}_1 \rangle]}{\partial t} + \nabla_{\mathbf{R}} \cdot [n(\mathbf{R}, t) \langle \mathbf{v}_1 \mathbf{v}_1 \rangle] - \frac{e\mathbf{E}}{m} n(\mathbf{R}, t) = -n(\mathbf{R}, t) \langle \mathbf{v}_1 \rangle \nu + \int_{\mathbf{v}_1} \mathbf{v}_1 \left(\frac{\partial n_1}{\partial t} \right)_S d\mathbf{v}_1, \quad (2.36)$$

where the jk -element of the direct product $\langle \mathbf{v}_1 \mathbf{v}_1 \rangle$ tensor is $v_1^{(j)} v_1^{(k)}$, the product of cartesian components $\{v_1^{(j)}, j = x, y, z\}$ of the velocity \mathbf{v}_1 .

In ion-ion recombination: (a) the recombination-sink rate is many orders of magnitude less than the collisional rate so that the sink term in (2.36) can be neglected in comparison with $n \langle \mathbf{v}_1 \rangle \nu$; (b) the characteristic time for substantial variation of $n(\mathbf{R}, t) \langle \mathbf{v}_1 \rangle$ is much longer than the mean time ν^{-1} between collisions so the time derivative in (2.36) is also negligible with respect to $n \langle \mathbf{v}_1 \rangle \nu$. Macroscopic diffusion is characterized by a flux vector $\mathbf{D} \cdot \nabla_{\mathbf{R}} n(\mathbf{R}, t)$ both in equilibrium (Maxwellian) and in non-equilibrium situations, where the diffusion (symmetric) tensor is

$$\mathbf{D} = \langle \mathbf{v}_1 \mathbf{v}_1 \rangle / \nu \quad (\text{cm}^2\text{s}^{-1}) \quad (2.37)$$

in terms of the averaged kinetic energy and collision frequency given in (2.33) or (2.35), while macroscopic drift is characterized by a flux vector $K\mathbf{E}n(\mathbf{R}, t)$ where the mobility is

$$K = e/m\nu \quad (\text{cm}^2\text{Stat V}^{-1}\text{s}^{-1}). \quad (2.38)$$

The ion-neutral collision frequency ν is central to both quantities. In thermal equilibrium, i.e. in the low E/N region where the thermal energy dominates the drift energy, $m \langle \mathbf{v}_1 \mathbf{v}_1 \rangle = (kT) \mathbf{1}$, where $\mathbf{1}$ is the unit tensor. When departures from spatial isotropy are dominated by the electric field \mathbf{E} , the diffusion tensor \mathbf{D} is diagonal with elements (D_L, D_T, D_T) , longitudinal L and transverse T to the field direction $\hat{\mathbf{E}}$. In thermal equilibrium these elements are equal so that the Einstein relation $(De = KkT)$ holds.

We now assume (c) that $\langle \mathbf{v}_1 \mathbf{v}_1 \rangle$ is R -independent, as in quasi-equilibrium when the phase-space distribution n_1 separates into a product $n_1(\mathbf{R}) n_{\mathbf{v}_1}(\mathbf{v}_1)$ of separate functions of \mathbf{R} and \mathbf{v}_1 as in the Maxwell-Boltzmann distribution (2.13a). Under assumptions (a)-(c), (2.36) provides the current

$$\mathbf{J}(\mathbf{R}, t) = n(\mathbf{R}, t) \langle \mathbf{v}_1 \rangle = -\mathbf{D} \cdot \nabla_{\mathbf{R}} n(\mathbf{R}, t) + K\mathbf{E}n(\mathbf{R}, t), \quad (2.39)$$

which together with the equation of continuity (2.30) implies

$$\begin{aligned} \frac{\partial n(\mathbf{R}, t)}{\partial t} + \nabla_{\mathbf{R}} \cdot [-D \cdot \nabla_{\mathbf{R}} n(\mathbf{R}, t) + K \mathbf{E} n(\mathbf{R}, t)] &= - \int_{\mathbf{v}_i} \left[\frac{\partial n_i(\mathbf{R}, \mathbf{v}_i, t)}{\partial t} \right] d\mathbf{v}_i \\ &\equiv - \sum_{i=-V(R)}^C \left[\frac{\partial n_i(\mathbf{R}, E_i, t)}{\partial t} \right]_S, \end{aligned} \quad (2.40)$$

in which the summation or integration over all states i between $-V(R)$ and C is equivalent to the \mathbf{v}_i -integration for spherical R -symmetry. On introduction of the null collision quantity,

$$\sum_{i=-A}^C \left\{ N_i^*(\mathbf{R}, E_i, t) \sum_{t=-A}^C k_{it}(R) - \sum_{t=-A}^C N_i^*(\mathbf{R}, E_t, t) k_{ti}(R) \right\} = 0, \quad (2.41)$$

where $-A$ is an arbitrary bound level, the sink term in (2.40) and given by (2.11) may be written as

$$\sum_{i=-V(R)}^C \left[\frac{\partial n_i}{\partial t} \right]_S = N \left[\sum_{i=-V(R)}^C N_i^*(\mathbf{R}, E_i, t) \sum_{t=-V}^C k_{it}(R) - \sum_{i=-V}^C \sum_{t=-M}^C N_i^*(\mathbf{R}, E_t, t) k_{ti}(R) \right] (4\pi R^2 N^+)^{-1}. \quad (2.42)$$

On integration of (2.40) over \mathbf{R} and with the aid of Gauss's theorem, of spherical symmetry and of (2.2), we have, on replacing \mathbf{E} by $-(\nabla V)/e$, the appropriate flux equation

$$\frac{\partial}{\partial t} \left[\int_0^R N^*(R, t) dR \right] - 4\pi R^2 \left[D \frac{\partial n(R, t)}{\partial R} + n(R, t) \frac{K \partial V}{e \partial R} \right] N^+ = -\alpha_3(R) n(R, t) N^+ \quad (2.43)$$

in terms of the net depletion (recombination) rate ($\text{cm}^{-3}\text{s}^{-1}$)

$$\alpha_3(R) n(R, t) N^+ = N \int_0^R dR \left\{ \sum_{i=-V}^C \left[N_i^*(\mathbf{R}, E_i, t) \sum_{t=-V}^C k_{it}(R) - \sum_{t=-M}^C N_i^*(\mathbf{R}, E_t, t) k_{ti}(R) \right] \right\}, \quad (2.44)$$

appropriate to the local (rather than asymptotic) density $n(R, t)$ of negative ions.

Subdivide the spectrum of internal energy into three regions: I, from C to some arbitrary bound level $-E$; II, from $-E$ to $-M$; and III, from $-M$ to $-V$. Regions I and II are interconnected by upward and downward collisional transitions and are inaccessible from region III which is therefore connected with I and II only through downward transitions. Introduce the inward diffusion-drift operator

$$\hat{\mathcal{J}}_1 = D \nabla + (K/e) \nabla V \equiv D \exp(-V/kT) \nabla \exp(V/kT), \quad (2.45)$$

such that the inward current j ($\text{cm}^{-2}\text{s}^{-1}$) is $\hat{\mathcal{J}}_1 n(R, t)$, and the flux operator \mathcal{D} which is such that the flux across the spheres each of radius R and surface area \mathcal{S} is

$$\mathcal{D}[4\pi R^2 N^+ n(R, t)] \equiv -N^+ \int_{\mathcal{S}} \mathbf{J} \cdot d\mathbf{S} \equiv 4\pi R^2 N^+ j(R, t). \quad (2.46)$$

Einstein's relation $D e = K k T$ has been used in (2.45) since the ions are in quasi-equilibrium with the field.

The contribution from region I to the left-hand side of (2.43) is therefore

$$-\frac{\partial}{\partial t} \left[\int_0^R N_I^*(R, t) dR \right] + \mathcal{D} N_I^*(R, t) = N \int_0^R dR \sum_{i=-E}^C \left(N_i^* \sum_{t=-V}^{-E} k_{it} - \sum_{t=-M}^{-E} N_i^* k_{ti} \right), \quad (2.47a)$$

on making use of the null collision relation (2.41) with $-A$ taken as $-E$, and where explicit dependences in the right-hand side are omitted. The right-hand side of (2.47a) is constant for $R \geq R_E$, the outermost turning point associated with $-E$, i.e. $V(R_E) = -E$. For region II,

$$-\frac{\partial}{\partial t} \left[\int_0^R N_{II}^*(R, t) dR \right] + \mathcal{D} N_{II}^*(R, t) = N \int_0^R dR \sum_{i=-M}^{-E} \left(N_i^* \sum_{t=-V}^C k_{it} - \sum_{t=-M}^C N_i^* k_{ti} \right), \quad (2.47b)$$

while for region III,

$$-\frac{\partial}{\partial t} \left[\int_0^R N_{III}^*(R, t) dR \right] + \mathcal{D} N_{III}^*(R, t) = -N \int_0^R dR \sum_{i=-V}^{-M} \sum_{t=-M}^C N_i^* k_{it}. \quad (2.47c)$$

For all three regions the number densities $N_i^*(R, E_i, t)$ on the right-hand side of (2.47) are solutions of the time-independent set (2.20) of coupled integro-differential equations. As previously noted, the left-hand side of (2.20) vanishes as R tends to the turning points $R(E_i)$ associated with bounded motion for a state of (negative) energy E_i . For the spectrum of bound levels in region II, it follows that the left-hand side of (2.20) does not depart appreciably from zero, particularly for levels $-E$ and $-M$ sufficiently close and deep, so that the radial extent of the associated bound orbits is minimal. Hence for region II, we have

$$N_i^*(R, E_i, t) \sum_{t=-V}^C k_{it}(R) \approx \sum_{t=-M}^C N_i^*(R, E_i, t) k_{it}(R); \quad -E \geq E_i \geq E_{-M}, \quad (2.48)$$

as for quasi-equilibrium at each R . Thus the right-hand side of (2.47b) vanishes in this approximation, in contrast to that for region I which includes the unbounded continuum and highly excited vibrational levels with large amplitudes of radial motion. Since all ion pairs with energy below $-E_M$ have recombined and are irretrievably lost to the recombination in progress, $N_i^*(R, (E_{-V} \rightarrow E_{-V}))$ vanishes, so that (2.48) implies, in the above approximation, that

$$\sum_{t=-M}^C N_i^*(R, E_i, t) k_{it}(R) \approx 0, \quad E_{-M} \geq E_i \geq E_{-V}, \quad (2.49)$$

which makes the right-hand side of (2.47c) vanish. This effectively zero rate is not difficult to establish since the collision rates k_{it} are relatively large only between neighbouring levels, which in this case are in a range surrounding $-M$ at which the number densities N_i^* of active ion pairs have already become much reduced from their equilibrium values (2.14) by the recombination process. Hence upon addition of 2.47 (a)-(c) over the three regions, the overall number density $N^*(R, t)$ satisfies

$$\begin{aligned} -\frac{\partial}{\partial t} \left[\int_0^R N^*(R, t) dR \right] - N^+ \int_{\mathcal{S}} \mathbf{J} \cdot d\mathbf{S} &= N \int_0^R dR \sum_{i=-E}^C \left(N_i^* \sum_{t=-V}^{-E} k_{it} - \sum_{t=-M}^{-E} N_i^* k_{it} \right) \\ &\equiv \alpha_3(R) n(R, t) N^+. \end{aligned} \quad (2.50)$$

Steady-state conditions can be maintained by continuous generation of ion pairs with infinite separation at an inward flux rate

$$F_x = -N^+ \int_{\mathcal{S} \rightarrow \infty} \mathbf{J} \cdot d\mathbf{S}$$

so that

$$-d(N^\pm)/dt + F_x = \alpha_3(R_E, t) n(R_E) N^+ = \alpha N^+ N^-, \quad (2.51)$$

where R_E is the maximum radius associated with collisional transitions across the energy level $-E$, i.e. $V(R_E) = -E$. Hence the steady-state recombination coefficient is,

$$\begin{aligned} \alpha &= \alpha_3(R_E) n(R_E) / N^- \\ &= \left(\frac{N}{N^+ N^-} \right) \int_0^{R_E} dR \sum_{i=-E}^C \left[N_i^*(R, E_i) \sum_{t=-V}^{-E} k_{it}(R) - \sum_{t=-M}^{-E} N_i^*(R, E_i) k_{it}(R) \right], \end{aligned} \quad (2.52)$$

where the number densities $N_i^*(R, E_i)$ are determined by appropriate solution of (2.20) subject to the boundary conditions (2.21). The solutions will, in general, depend on gas density N , and α

is then a general function of N . We note that (2.51) equates the steady-state inward flux αN^- or $4\pi R^2 \hat{J}_1 n$ with $\alpha_3(R_E) n(R_E)$ which is the net rate of reaction within R_E . Thus (2.51) and (2.52) manifest quite clearly a partially absorbing boundary condition at R_E around which the ion density is continuous.

In summary we have obtained in this section the necessary equation (2.20) for solution of $N^+(R, E, t)$, and the appropriate equation (2.50) or equivalent expression (2.52) for the recombination coefficient α from the appropriate flux equation (2.43), a combination of a derived momentum equation (2.36) and the equation of continuity (2.30).

2.3. Steady-state solution

As $R \rightarrow R_E$ and beyond, $N^+ F_c(R)$, the right-hand side of the flux (2.50) becomes constant. Let the ion-density $N^+(R, t)$ decay as $N^+(R) \exp(-At)$ so that (2.50) reduces, with the aid of (2.51), to

$$\begin{aligned} N^+ F_c(R_E) &= AN^+ \int_0^R 4\pi R^2 n^-(R) dR + 4\pi R^2 N^+ D \exp(-V/kT) \frac{\partial}{\partial R} [n^-(R, t) \exp(V/kT)] \\ &= \alpha_3(R) n^-(R) N^+ = \alpha N^+ N^-, \quad R \geq R_E. \end{aligned} \quad (2.53)$$

where $n^-(R)$ denotes the density of negative ions.

The steady-state solution of (2.50) involves neglect in (2.53) of the A -term which depends on $n^-(R)$ within R_E . This neglect implies

$$\int_0^{R_E} 4\pi R^2 n^-(R) dR \ll 1 \quad (2.54a)$$

since $A \sim \alpha N^-$, such that

$$N^- \ll (\frac{4}{3}\pi R_E^3)^{-1}, \quad (2.54b)$$

i.e. few unreacted ions must be present in the 'recombination volume' as measured by the R_E -sphere in order that the frequency decay constant A may be neglected. Given $R_E \sim e^2/kT$ for example, appropriate to a bound level at kT below the dissociation limit, $N^\pm \ll 10^{16} \text{ cm}^{-3}$ for validity, while smaller R_E (as at high N) will extend the limits to higher N^\pm . Integration of (2.53) under the steady-state condition then yields

$$N^- - n^-(R) \exp(V/kT_{\text{eff}}) = [F_c(R_E)/\alpha_h] P(R), \quad R \geq R_E, \quad (2.55)$$

where $\alpha_h = 4\pi D R_E$, the high density Langevin limit (1.2);

$$P(R) = R_E \int_R^\infty \exp(V/kT_{\text{eff}}) dR/R^2, \quad (2.56)$$

is an important function related to the probability (§2.4) that the R -ion pair expands by diffusional drift to infinite separation; and

$$R_e = e^2/(De/K) \equiv e^2/kT_{\text{eff}}, \quad (2.57)$$

is the natural unit of length. At low E/N when the thermal energy dominates the drift energy, thermal equilibrium at temperature T is obtained, and the Einstein relation $De = KkT$ or, equivalently, $DR_e = Ke$, holds such that T_{eff} in (2.55) and (2.56) is simply T . The steady-state negative-ion density outside R_E can, with the aid of (2.53) be written in two equivalent forms:

$$n^-(R) = N^- \exp(-V/kT) \left[1 - \frac{\alpha}{\alpha_h} P(R) \right] = \frac{N^- \exp[-V(R)/kT] [\alpha_h/P(R)]}{\alpha_3(R) \exp[-V(R)/kT] + \alpha_h/P(R)}, \quad R \geq R_E, \quad (2.58a)$$

in which T_{eff} is denoted here by T for brevity;

$$n^-(R) = N^- \exp(-V/kT) \exp\left[-\frac{R_e}{\alpha_h} \int_R^\infty \alpha_3(R) R^{-2} dR\right]. \quad (2.58b)$$

Hence the overall recombination coefficient α from (2.53) is

$$\alpha = \alpha_3(R_E) n^-(R_E) / N^- = \frac{\alpha_3(R_E) \exp[-V(R_E)/kT] [\alpha_h/P(R_E)]}{\alpha_3(R_E) \exp[-V(R_E)/kT] + \alpha_h/P(R_E)} = \text{const.} \quad (2.59)$$

in terms of α_h which is known, and of $\alpha_3(R_E)$ which is yet to be determined. Since α_3 is internally dependent on the phase densities, $N_1^*(R, E_1)$, through (2.44), we note that α , with this required knowledge of N_1^* , may, of course, be determined directly from (2.52) rather than from (2.59). However, not only does (2.59) promote further physical and basic understanding of recombination, but it is also very effective when alternative means are used to deduce $\alpha_3(R_E)$, as, for example, in § 4.2. Steady-state conditions are also achieved at $R > R_E$ effectively instantaneously for low N , and after time lapse $t \gg R_E^2/D$ for high N (see § 2.5), and are independent of condition (2.54b).

Since $\alpha_h \sim N^{-1}$, from (2.58), at low gas densities N ,

$$n^-(R) \approx N^- \exp[-V(R)/kT], \quad R \geq R_E, \quad (2.60)$$

the Boltzmann distribution, such that (2.59) tends at low N to

$$\alpha_{10} = \alpha_3(R_E) \exp[-V(R_E)/kT] \equiv \alpha_{rn}(R_E), \quad (2.61)$$

which is from (2.53) the recombination coefficient that would pertain provided the Boltzmann ion-distribution were maintained (as at low N), i.e. α_{rn} in the absence of net ionic transport (as in a Boltzmann distribution) measures the rate of reaction within R_E . Thus, (2.59) reads,

$$\alpha = \alpha_{rn} \alpha_{tr} / (\alpha_{rn} + \alpha_{tr}), \quad (2.62)$$

where the recombination coefficient α_{tr} at high gas densities is,

$$\alpha_{tr} = 4\pi D \int_{R_E}^\infty \exp(KV/De) R^{-2} dR = [\alpha_h/P(R_E)] \equiv \alpha_{tr} \quad (2.63)$$

the rate of ion transport by diffusional-drift. Hence, the ion number density (2.58) is

$$n^-(R) = N^- \exp(-V/kT) \left[1 - \frac{\alpha}{\alpha_{tr}} \frac{P(R)}{P(R_E)}\right], \quad R \geq R_E. \quad (2.64)$$

At high N , therefore, $n^-(R)$ from (2.64) departs significantly from the Boltzmann distribution at $R \approx R_E$, where the reactivity of the ion pairs is strong; and at low N , n^- is approximately Boltzmann where the reactivity is weak. As N is increased, the reactivity of the ion pairs (resulting from 'effective' collisions in the increasingly dense gas) becomes so great compared with the rates of ionic transport that continued reaction causes significant depletion in the ionic concentration in a localized region, and the ion R -distribution from (2.64) is far from Boltzmann. This feature is, in general, responsible for the failure of the use of equilibrium kinetics (partition functions, etc.) or of equilibrium concentrations of reactants for rates of chemical reactions in a dense medium, in contrast to that evident for low density gases (see (2.60)). It is also this feature that invalidates the *ab initio* use of the Debye-Hückel interaction, appropriate only for equilibrium situations at asymptotic R , so as to acknowledge possible plasma sheathing effects when the ion densities N^\pm are raised from 10^8 cm^{-3} to about 10^{14} cm^{-3} . Use of an interaction, self-consistent with the ionic distribution and recombination sink, is the correct procedure (see § 4).

We note that α_3 and hence α_{10} contain, in general, a complicated dependence on N through (2.44) and (2.20). The overall recombination rate (2.59) is, therefore, controlled by the rate-limiting step of the rate of ionic transport, as measured by α_{tr} , and of the rate of ion-ion reaction (by effective three-body collisions), as measured by α_{rn} . Thus, the full theoretical development of the relation (2.62) has provided basic insight into a relation previously suspected (Bates & Flannery 1969), of one that is useful when the rate α_{rn} of reaction can be deduced without explicit knowledge of the phase densities $N_i^*(R, E_i)$, as in § 4.2.

The physical significance of $P(R)$ in (2.63) and in (2.64) where it provides the R -variation of the departure of $n^-(R)$ from pure Boltzmann is made apparent in the following subsection; further study is also made of the separation of recombination into its transport-rate and reaction-rate components.

2.4. Partially absorbing and fully absorbing sinks: transport and reaction rates

The time-dependent continuity equation (2.40) is

$$\frac{\partial n^-(R, t)}{\partial t} + \nabla_R \cdot \mathbf{J} = - \sum_{i=-V}^C \left[\frac{\partial n_i(R, E_i, t)}{\partial t} \right]_S, \quad (2.65)$$

where the current vector (number of ions per second crossing unit area of an R -sphere)

$$\mathbf{J} = -D[\nabla n^-(R, t) + n^-(R, t) \nabla(V/kT)] \equiv -D \exp(-V/kT) \{d[n^- \exp(V/kT)]/dR\} \hat{\mathbf{R}}, \quad (2.66)$$

arises from diffusional drift of the ions with relative diffusion coefficient D in the gas Z under an external spherically symmetric field of potential $V(R)$. The sink term (2.11) has been shown to be,

$$\alpha_3(R, t) n^-(R, t) N^+ = N \int_0^R dR \left\{ \sum_{i=-E}^C \left[N_i^*(R, E_i, t) \sum_{j=-V}^{-E} k_{ij}(R) - \sum_{j=-M}^{-E} N_i^*(R, E_i, t) k_{ji}(R) \right] \right\}. \quad (2.67)$$

which equates the frequency of production of R -ion pairs by diffusional drift to the frequency of ion reaction within R .

Although the phase-space densities $n_i(R, E_i, t)$ are in principle solutions of the appropriate time-dependent Boltzmann equation (2.12), important progress can be achieved upon assumption of either an instantaneous reactive sink or a partially absorbing sink that operates for ion pairs with internal separations $R \leq S$. Also, the physical meaning of P in (2.63) becomes apparent. Thus (2.65) is equivalent, with $\mathbf{j} \equiv -\mathbf{J}$, to,

$$\frac{\partial n^-}{\partial t} - \frac{1}{R^2} \frac{\partial(R^2 \mathbf{j})}{\partial R} = 0, \quad (2.68)$$

solved subject to prescribed boundary conditions that characterize the sink under different gas densities.

The steady-state solutions at R_1 and R_2 therefore satisfy

$$[n^-(R) \exp(V/kT)]_{R_1}^{R_2} = (F/4\pi D) [P(R_1) - P(R_2)], \quad (2.69)$$

where $P(R)$ is given by (2.56) and F is the steady-state constant inward flux $4\pi R^2 \mathbf{j}$. For ion pairs that react (neutralize) instantaneously within the sink S , as at high N ,

$$\left. \begin{aligned} n^-(R, t) &= 0, & R &\leq S, \\ n^-(R, t) &= N^-, & R &\rightarrow \infty \end{aligned} \right\} \quad (2.70)$$

such that (2.68) yields,

$$\alpha_{tr} = \alpha_{nl} = F/N^- = 4\pi D \int_S^\infty \exp(V/kT) dR/R^2, \quad (2.71)$$

the transport rate, which at high N is equivalent to the recombination rate. This reduces to

$$\alpha_d = 4\pi DS \quad (2.72)$$

when the interaction V between the ions is neglected, and to

$$\alpha_{bl} = 4\pi DR_c/[1 - \exp(-R_c/S)], \quad (2.73)$$

for pure coulomb attraction

$$V/kT = -Z_1 Z_2 e^2 / RkT \equiv -(R_c/R) \quad (2.74)$$

between ions of charge $Z_1 e$ and $-Z_2 e$.

For recombination in a gas, (2.72) and (2.73) are the diffusion and diffusional-drift results of Harper (1932) and of Bates (1975) respectively. For coagulation of colloid suspensions in a liquid of permittivity ϵ , analogous expressions (with $R_c = Z_1 Z_2 e^2 / \epsilon kT$) have been obtained by Smoluchowski (1917) and by Debye (1942). For this reason the full time-dependent equation (2.68) for a spherical field is frequently referenced as the Debye-Smoluchowski equation, derived originally by Smoluchowski (1916, 1917) from a stochastic random-walk picture of the process. The interesting feature is that it is a natural consequence of the basic microscopic treatment, which therefore provides its full generalization (2.65) and (2.67) to an arbitrary compressible sink based on detailed collisional kinetics which in turn depend on the phase-space densities $n_i(R, E_i, t)$. However, with this knowledge of n_i , the steady-state α can be obtained directly from (2.52), rather than from the solution of (2.65).

It is interesting to note from comparison of (2.72) and (2.73) that proper account of the interaction field is acknowledged simply by replacing S in the field-free case (2.72) by $R_c/P(S)$; and that (2.72) alone is incorrect if realistic $S \propto (R_c/N)^{1/2}$ (see § 4.2) are adopted. As N is increased, it is obvious that the three-body reaction zone must decrease and cannot be arbitrarily held at R_c to ensure identity between (2.72) and the correct limit (2.73). This note helps resolve previous confusion that existed (see Flannery 1976, p. 423) between treatments based either on pure diffusion (Harper 1932) or on pure mobility (Langevin 1903). Neither treatment is rigorously correct: mobility and diffusion effects must be coupled as in (2.71), although *only* for pure Coulomb attraction any error in Langevin's derivation disappears in the high- N limit unlike that involved with (2.72). This coupling also ensures thermodynamic equilibrium between effects of mobility and diffusion and is very important to the general determination of the phase-space densities (§ 5.2) at intermediate and high N .

A correlation can be established between two problems differing only in the generation boundary condition, i.e. between the recombination rate α for the homogeneous case where the process is driven by the boundary condition (2.70) for $n(R \rightarrow \infty)$ and the probability $\mathcal{P}^c(R_0, R_E)$ for the diffusional-drift contraction of ions generated at R_0 . Between R_0 and an instantaneous sink at $R_E < R_0$, (2.69) then yields

$$n^-(R) \exp(V/kT) = (F_c/4\pi D) [P(R_E) - P(R)], \quad R_E \leq R \leq R_0, \quad (2.75)$$

where F_c is the net inward flux at R . In the presence of a sink at infinity,

$$n^-(R) \exp(V/kT) = (F_c/4\pi D) P(R), \quad R_0 \leq R \leq \infty, \quad (2.76)$$

where F_o is the net outward flux at R . The probability that an isolated R_0 -ion pair contracts by diffusional-drift is

$$\mathcal{P}_{(s)}^c(R_0, R_E) = F_c(R_0)/[F_o(R_0) + F_c(R_0)] = P(R_0)/P(R_E), \quad (2.77a)$$

where the subscript (s) denotes that this \mathcal{P}^c pertains only to the case of spontaneous reaction. The probability that it expands (by diffusion against the force of attraction enhanced by the presence of the sink) to infinite internal separation is

$$\mathcal{P}_{(s)}^c(R_0, R_E) = F_e(R_0)/[F_e(R_0) + F_c(R_0)] = 1 - P(R_0)/P(R_E). \quad (2.78a)$$

Thus, in the homogeneous case the negative ion density (2.58) can be rewritten as

$$n^-(R) = N^- \exp(-V/kT) [1 - (\alpha/\alpha_{tr}) \mathcal{P}_{(s)}^c(R, R_E)] \xrightarrow{N \rightarrow \infty} N^- \exp(-V/kT) \mathcal{P}_{(s)}^c(R, R_E), \quad (2.79a)$$

where $\mathcal{P}_{(s)}^c$ is interpreted as the probability of diffusional escape of an R -ion to infinity in the presence of an instantaneous sink at R_E , and yields the fractional departure of $n^-(R)$ from pure Boltzmann at high N .

Hence the recombination rate at high N is the transport rate

$$\alpha_{tr} = 4\pi R_E^2 D \exp(-V/kT) [\partial \mathcal{P}_{(s)}^c(R, R_E)/\partial R]_{R_E} = \alpha_h/P(R_E), \quad (2.80a)$$

where α_h is the Langevin rate $4\pi D R_E$ and $\mathcal{P}_{(s)}^c$ is the probability of contraction from R to R_E against diffusional escape. Thus, the physical origin of P in the transport rate (2.63), which is identical to the recombination rate at high N , is now apparent. For pure coulomb attraction at high N when the sink radius $R_E \ll R_e$, the escape and recombination probabilities reduce to

$$\mathcal{P}_{(s)}^c(R) \sim \exp(-R_e/R), \quad (2.81a)$$

and

$$\mathcal{P}_{(s)}^c(R) \sim 1 - \exp(-R_e/R) \quad (2.81b)$$

in agreement with Onsager (1938), and $n^-(R) \approx N^- \exp(-V/kT) \exp(-R_e/R)$.

Extension of the rate (2.73), valid only for instantaneous reaction after ion approach by mobility-diffusion, to lower gas densities N can be achieved by solving (2.68) subject to the more accurate boundary condition

$$j(R, t) = \Gamma_3 n^-(R, t), \quad R = S, \quad (2.82)$$

where $\Gamma_3(R)$ is the speed of reaction of R -ion pairs. This (radiation or partial absorption) condition acknowledges the finite rate of reaction (by three-body effective collisions) after ion approach and implies a probability for subsequent diffusional-drift expansion of the unreacted ion pairs; if Γ_3 is infinitely fast as at high N then (2.70) is recovered. The diffusion-drift equation (2.68) governs ion transport up to S from which the ion departs inward with an effective finite speed $\Gamma_3(S)$ towards certain recombination within S , the radius that characterized the transition from transport (i.e. ineffective collisions) alone to reaction (i.e. effective collisions). Since

$$F = 4\pi R^2 j = (4\pi R^2 \Gamma_3) n^-(R, t) = \alpha(t) N^-, \quad (2.83)$$

then, provided Boltzmann equilibrium conditions for the ions are maintained, the recombination coefficient (F/N^-) would be

$$\alpha_{rn} = (4\pi R^2 \Gamma_3) \exp(-V/kT) \equiv \alpha_3(R) \exp(-V/kT), \quad (2.84)$$

where we are reminded of the role of the finite rate of three-body energy-change collision (the reaction rate) by attaching 3 as a subscript to both α and Γ .

Hence, (2.82) is simply

$$\alpha_3(S) n^-(S, t) = 4\pi S^2 j(S, t) = \alpha N^-, \quad (2.85)$$

which equates the *finite* collisional recombination rate within S to the flux of production of S -ion pairs. The basis of this radiation condition (2.82) or (2.85) has already been established

theoretically by (2.52). Thus the steady-state solution of (2.68) for the ion density subject to (2.82) or (2.85) is

$$n^-(R, t \rightarrow \infty) = N^- \exp(-V/kT) \left[1 - \frac{\alpha}{\alpha_{tr}} \frac{P(R)}{P(S)} \right] \quad (2.86)$$

which yields the following steady-state recombination coefficient:

$$\alpha(t \rightarrow \infty) = \frac{\alpha_3(S) \exp(-V(S)/kT) \alpha_{tr}}{\alpha_3(S) \exp(-V(S)/kT) + \alpha_{tr}} \equiv \frac{\alpha_{rn} \alpha_{tr}}{\alpha_{rn} + \alpha_{tr}} \quad (2.87a)$$

in agreement with the results (2.64) and (2.58) of the previous subsection.

For this case of finite reaction, a relation between α for the homogeneous case (with source only at infinity), and the contraction and escape probabilities $\mathcal{P}^{c,e}(R, R_E)$ for the case where ion-pairs are continuously generated with internal separation R , can be obtained, as before, from (2.69) to yield

$$\text{and } \mathcal{P}^c(R, R_E) = \frac{[n^-(R) - (\alpha/\alpha_{rn}) N^- \exp(-V/kT)] P(R)}{n^-(R) P(R_E) - (\alpha/\alpha_{rn}) N^- \exp(-V/kT) P(R)} \xrightarrow{\alpha_{rn} \gg \alpha} \frac{P(R)}{P(R_E)} \quad (2.77b)$$

$$\mathcal{P}^e(R, R_E) = \frac{P(R_E) - P(R)}{P(R_E) - (\alpha/\alpha_{rn}) N^- \exp(-V/kT) P(R)/n^-(R)} \xrightarrow{\alpha_{rn} \gg \alpha} 1 - \frac{P(R)}{P(R_E)}. \quad (2.78b)$$

The number density of ion pairs generated with internal separations in the interval dR about R is $4\pi R^2 n^-(R) N^+ dR$.

When n^- is given by (2.86) with $S = R_E$ then

$$\mathcal{P}^c(R, R_E) = \frac{\alpha}{\alpha_{tr}} \frac{P(R)}{P(R_E)} \equiv 1 - \mathcal{P}^e(R, R_E), \quad (2.77c)$$

so that

$$n^-(R) = N^- \exp(-V/kT) \mathcal{P}^e(R, R_E) \quad (2.79b)$$

and

$$\alpha = 4\pi R_E^2 D \exp(-V/kT) [\partial \mathcal{P}^c / \partial R]_{R_E}, \quad (2.80b)$$

which are the direct generalizations of (2.79a) and (2.80a) to finite reaction. Thus \mathcal{P}^e , in general, may be interpreted as the fractional departure of the ion density from Boltzmann equilibrium and is the solution of $\nabla \cdot \{\exp(-V/kT) \nabla \mathcal{P}^e\} = 0$ subject to $\mathcal{P}^e(\infty) \rightarrow 1$ and $D(\partial \mathcal{P}^e / \partial R) = \Gamma_3 \mathcal{P}^e$ at R_E . Hence (2.85) and (2.87a) may be rewritten as

$$\alpha = \mathcal{P}_r \alpha_{tr} = \mathcal{P}^e(R_E, R_E) \alpha_{rn} \quad (2.87b)$$

where the probability of recombination

$$\mathcal{P}_r = \alpha_{rn} / (\alpha_{rn} + \alpha_{tr}) = \mathcal{P}^c(R_E, R_E) \rightarrow \begin{cases} \alpha_{rn} / \alpha_{tr}, & \alpha_{rn} \ll \alpha_{tr}, \\ 1, & \alpha_{rn} \gg \alpha_{tr}, \end{cases} \quad (2.77d)$$

is simply the contraction probability for ion pairs generated with internal separations equal to the sink radius, i.e. $\mathcal{P}_r \leq 1$ is the probability of intrapair (geminate) recombination.

Note that the boundary condition (2.85) is essentially identical with the exact condition (2.52) based on detailed kinetics when R_E is identified with S . This boundary condition can be suitably incorporated by rewriting the time-dependent Debye-Smoluchowski equation (2.68) as

$$-\frac{\partial n^-}{\partial t} + \nabla \cdot \mathbf{j} = \Gamma_3 n^- \delta(R - S) = \alpha_3 n^- \delta(R - S), \quad (2.88a)$$

which uniquely identifies the strength of the sink as the speed of three-body recombination; for Γ_3 large compared with the rate of ionic transport, the reactivity of the sink is effectively instantaneous, and α is given then by (2.73); while (2.87) pertains when Γ_3 is comparable with the ion transport rate. No deactivating reaction implies zero Γ_3 , and hence zero rate of recombination.

The number density N_i of all ion pairs AB with internal separation $R \geq S$ then decays at a rate

$$\begin{aligned} -\frac{dN_i}{dt} &= -\frac{\partial}{\partial t} \int_S^\infty 4\pi R^2 N^+ n^-(R, t) dR = [4\pi S^2 \Gamma_3 n^-(S, t) - \{F_\infty - 4\pi S^2 j(S - \epsilon, t)\}] N^+ \\ &= \alpha(t) N^+ N^- - F_\infty N^+, \end{aligned} \quad (2.88b)$$

where F_∞ is the rate (s^{-1}) of generation of negative ions at infinity, and α is the time-dependent rate ($cm^3 s^{-1}$) of recombination appropriate to asymptotic ion densities N^\pm . If the ion current approaching S is absorbed by reaction within S , then $\lim_{\epsilon \rightarrow 0} j(S - \epsilon, t) \rightarrow 0$. In steady state, the rate $4\pi R^2 j(R, t)$ from (2.88a) is constant for $R \geq S + \epsilon$ and equals both the production and absorption rates F_∞ and $4\pi S^2 \Gamma_3 n^-$, respectively, in (2.88b).

In conclusion, this subsection has emphasized the decomposition of the recombination rate α into its reaction and transport components, α_{rn} and α_{tr} , respectively, which act in series so that $\alpha = \mathcal{P}_r \alpha_{tr}$ in terms of the recombination probability \mathcal{P}_r of (2.77d), and is determined by the rate limiting step α_{rn} or α_{tr} in the limit of low N and high N respectively. Also the relation has been developed between α and \mathcal{P}_r for the homogeneous case with the escape probability \mathcal{P}_e of ions generated within the medium. Steady-state recombination can therefore be regarded as being maintained either by a continuous source in ions at infinity or by a source that generates within the medium R -ion pairs with density (2.86). In the latter picture, the recombination probability \mathcal{P}_r is simply the probability \mathcal{P}_c for contraction of those geminate R_E ion pairs so generated. Also proper contact has been established between the microscopic treatment and the generalized Debye-Smoluchowski equation (2.88a) which blends the macroscopic phenomena of diffusional-drift (which is characterized by the departure from pure classical ion-ion trajectories to a zigzag statistical pattern) and reaction between individual ion pairs. The sink in (2.88a) is compressible in the sense that its radius S is determined by collisional kinetics, which depends on the gas density N , as explicitly shown in § 4.2 where S is shown to contract from *ca.* R_E to *ca.* $(R_E \lambda_r)^{1/2}$ as N is increased.

2.5. Analytical solution of the time-dependent generalized Debye-Smoluchowski equation

Equation (2.65) is frequently called by those interested in coagulation in colloid solutions the Debye-Smoluchowski equation after the original authors who found its steady-state solution for the field-free case ($V = 0$) and a coulomb interaction respectively, appropriate to an instantaneous sink ($\mathcal{P}_r \rightarrow 1$ or $V \rightarrow \infty$). While an exact time-dependent solution can be immediately obtained in the field-free case, there has as yet been no exact solution obtained for a general interaction V , although a large body of literature exists on various analytical approximations for the coulomb interaction. These are based on Green functions, perturbation expansions, 'prescribed' diffusion, etc. (Mozumder 1968, Abell & Mozumder 1972, Abell *et al.* 1972, Magee & Tayler 1972), and on the Mathieu equation (Hong & Noolandi 1978) via the resemblance between (2.65) for the coulomb interaction and the Schrödinger equation with an R^{-4} -potential. It may also, of course, be solved by numerical procedures (Freed & Pedersen 1976).

The generalized equation (2.88a) is of basic significance not only to ion-ion and atom-atom recombination in a gas and in dilute ionic solutions, but also to medical radiology and to diffusion- and field-controlled reactions in metabolizing systems (as enzyme-substrate reactions in a cell (Reid 1952)). It is of general importance in theoretical physics. In this section, we present an

approximate yet accurate analytical time-dependent solution, and associated recombination rates, of the equation

$$\frac{\partial n(R, t)}{\partial t} = \frac{1}{R^2} \frac{\partial}{\partial R} (R^2 j) \quad (2.89a)$$

with a general diffusional-drift current

$$j(R, t) = D \exp(-V/kT) \partial [n(R, t) \exp(V/kT)] / \partial R. \quad (2.89b)$$

Our basic equation (2.50) derived from microscopic principles is, in effect, equivalent to (2.89) solved subject to certain boundary conditions.

The boundary conditions are

$$n(R \rightarrow \infty, t) = N^- \exp(-V/kT), \quad (2.90)$$

the Boltzmann distribution, for continuous generation of ions at infinity, and, either

$$n(R, t) = 0, \quad R \leq S, \quad (2.91a)$$

for an instantaneous sink within a sphere of radius S , or

$$\Gamma_3 n(S, t) = j(S, t), \quad (2.91b)$$

for a partially absorbing sink where Γ_3 is, as before, the speed of (three-body) reaction for ion pairs brought to internal separation S by ion transport such that

$$\alpha_3 = 4\pi S^2 \Gamma_3. \quad (2.91c)$$

The initial ($t = 0$) distribution

$$n(R, t = 0) = N^- \exp(-V/kT), \quad (2.92)$$

is assumed Boltzmann. Two examples follow below.

(a) *Field-free case*, $V = 0$. Although the exact diffusion-controlled solution ($V = 0$) is known (Reid 1952), being analogous to heat conduction through a sink, we include it here for use in the case of general $V(R)$. Introduce the dimensionless quantities

$$r = R/S - 1, \quad \tau = Dt/S^2, \quad (2.93)$$

and let

$$n'(R, t) = (R/S) n(R, t), \quad (2.94)$$

such that (2.89) with $V = 0$ reduces to

$$\partial n'(r, \tau) / \partial \tau = \partial^2 n'(r, \tau) / \partial r^2. \quad (2.95)$$

This equation can be solved directly by the method of Laplace transformation to give

$$n_d^{(s)}(R, t) = N^- \{1 - (S/R) \operatorname{erfc}[(R-S)/2(Dt)^{1/2}]\}, \quad (2.96)$$

appropriate to diffusion (d) controlled transport and spontaneous (s) reaction for an initial random distribution N^- , where the error function (or probability integral)

$$\operatorname{erfc} \chi = \frac{2}{\sqrt{\pi}} \int_{\chi}^{\infty} \exp(-\chi^2) d\chi. \quad (2.97)$$

The rate of recombination for this case ($V = 0$) is

$$\alpha_d^{(s)}(t) = 4\pi S^2 j(S, t) / N^- = \alpha_d [1 + S/(\pi Dt)^{1/2}], \quad (2.98a)$$

where

$$\alpha_d = 4\pi SD \quad (2.98b)$$

is the steady-state ($t \rightarrow \infty$) solution (2.72) obtained by Smoluchowski (1917) for coagulation in colloid solutions and by Harper (1932) for ion-ion recombination in a gas. The rate of decrease in the number \mathcal{N}_R of diffusing species outside S can be evaluated directly from,

$$\frac{d\mathcal{N}_R}{dt} = N^- \frac{d}{dt} \int_S^\infty 4\pi SR \operatorname{erfc}[(R-S)/2(Dt)^{1/2}] dR = \alpha_d^{(s)} N^-, \quad (2.99)$$

where the derived $\alpha_d^{(s)}$ is identical with (2.98), as expected from (2.89a). Under the condition (2.91b) for finite (f) reaction and diffusive transport,

$$n_d^{(f)}(R, t) = N^- \{1 + (\alpha/\alpha_d) (S/R) [\exp(2\Omega\chi) \exp \chi^2 \operatorname{erfc}(\chi + \Omega) - \operatorname{erfc} \Omega]\}, \quad (2.100)$$

where the time dependence is contained in

$$\chi(t) = (1 + \alpha_3/\alpha_d) (Dt)^{1/2}/S \equiv (\alpha_3/\alpha) (Dt)^{1/2}/S, \quad (2.101)$$

and in

$$\Omega(t) = (R-S)/2(Dt)^{1/2}, \quad (2.102)$$

which vanishes at the sink, and

$$\alpha = \alpha_3 \alpha_d / (\alpha_3 + \alpha_d) \quad (2.103)$$

in terms of (2.91c) and (2.99). When the rate α_3 of reaction is much larger than the rate α_d of ion transport, $\chi \rightarrow \infty$, $\alpha = \alpha_d$, the limiting rate, and (2.96) is recovered from (2.100). The time-dependent recombination rate from the radiation condition (2.91b) with (2.100) is

$$\alpha_d^{(f)}(t) = \alpha_3 n_d^{(f)}(S, t) / N^- = \alpha [1 + (\alpha_3/\alpha_d) \exp \chi^2 \operatorname{erfc} \chi], \quad (2.104)$$

and α is therefore the steady-state ($t \rightarrow \infty$) solution (since $\operatorname{erfc} \rightarrow 0$). The rate (2.104) also follows directly from $4\pi S^2 D (dn_d/dR)_S$ as expected from (2.91b). At $t = 0$ the recombination rate $\alpha_d^{(f)}(0)$ is simply the rate α_3 of reaction, as expected, since an initial ion distribution N^- has been assumed. Note that (2.98) for the instantaneous sink yields an infinite recombination rate, at $t = 0$, again as expected from the assumed infinite rate of reaction.

(b) *General field V*: The following analytical solution is based on the novel transformation from R to the variable

$$\tilde{R} = \left\{ \int_R^\infty \exp[V(R)/kT] \frac{dR}{R^2} \right\}^{-1}; \quad \frac{d\tilde{R}}{dR} = \left(\frac{\tilde{R}}{R} \right)^2 \exp(V/kT), \quad (2.105)$$

a transformation not without its physical significance. It is related to the probability $\mathcal{P}_{(s)}^c$ in (2.77a) that an R_0 -ion pair will further contract by diffusion under V , in the presence of an *instantaneous sink* at S (or else to the diffusional expansion against V to infinite separation), i.e. (2.77a) is rewritten with the aid of (2.105) as

$$\mathcal{P}_{(s)}^c(R_0, S) = \tilde{R}(S)/\tilde{R}(R_0) = \tilde{S}/\tilde{R}_0. \quad (2.106)$$

Let

$$n_V(R, t) = n(R, t) \exp(V/kT), \quad (2.107)$$

such that (2.89) becomes

$$\frac{\partial n_V(\tilde{R}, t)}{\partial t} = \frac{\tilde{D}}{\tilde{R}^2} \frac{\partial}{\partial \tilde{R}} \left[\tilde{R}^2 \frac{\partial n_V(\tilde{R}, t)}{\partial \tilde{R}} \right], \quad (2.108)$$

where the transformed diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$) is

$$\tilde{D} = D(dR/d\tilde{R})^2. \quad (2.109)$$

The form of this equation is, in the transformed \tilde{R} -representation, identical with that for the field-free case in the original R -representation. Accordingly, introduce scaled quantities (2.93) and

$$\tilde{r} = (\tilde{R}/\tilde{S}) - 1, \quad \tilde{\tau} = \tilde{D}t/\tilde{S}^2, \quad n' = (\tilde{R}/\tilde{S}) n_V(\tilde{R}, t) \quad (2.110)$$

such that (2.108) reduces to

$$\frac{\partial n'(\tilde{r}, \tilde{\tau})}{\partial \tilde{\tau}} = \left(\frac{d\tilde{r}}{d\tilde{\tau}}\right)^2 \frac{\partial^2 n'(\tilde{r}, \tilde{\tau})}{\partial \tilde{r}^2} = \frac{\partial^2 n'}{\partial \tilde{r}^2} + \left\{ \left(\frac{d\tilde{r}}{d\tilde{\tau}}\right)^2 \frac{d^2 \tilde{r}}{d\tilde{\tau}^2} \right\} \frac{\partial n'}{\partial \tilde{r}} \quad (2.111a)$$

which suggests the following two procedures for solution. Assume $(d\tilde{r}/d\tilde{\tau})$ remains constant such that introduction of \tilde{r} of (2.110) yields

$$\frac{\partial n'(\tilde{r}, \tilde{\tau})}{\partial \tilde{\tau}} = \frac{\partial^2 n'(\tilde{r}, \tilde{\tau})}{\partial \tilde{r}^2} \quad (2.111b)$$

which is the field-free diffusion equation in $\tilde{r}, \tilde{\tau}$ -space. Alternatively, since

$$\left(\frac{d\tilde{r}}{d\tilde{\tau}}\right)^2 \frac{d^2 \tilde{r}}{d\tilde{\tau}^2} = -S \left[\frac{2\tilde{R}}{\tilde{R}^2} \exp(V/kT) - \frac{2}{\tilde{R}} + \frac{\partial}{\partial \tilde{R}} (V/kT) \right] \quad (2.112)$$

in the right-hand side of (2.111a) vanishes to $O(R^{-3})$ for the Coulomb interaction and is negligible for $R^3 \geq R_{\min}^3 = S(e^2/kT)^2$,

$$\frac{\partial n'(r, \tau)}{\partial \tau} = \frac{\partial^2 n'(r, \tau)}{\partial r^2}, \quad (2.111c)$$

the one-dimensional diffusion equation in r, τ -space.

The full solution of (2.89) appropriate to spontaneous reaction (2.91a) is therefore, after some analysis, of (2.111b),

$$n^{(s)}(R, t) = N^- \exp(-V/kT) \left\{ 1 - \frac{\tilde{S}}{\tilde{R}} \operatorname{erfc} \left[\frac{(\tilde{R} - \tilde{S}) d\tilde{R}}{2(Dt)^{1/2} d\tilde{R}} \right] \right\}. \quad (2.113)$$

The recombination rate then reduces to

$$\alpha^{(s)}(t) = 4\pi S^2 j(S, t) / N^- = \alpha_{tr} \left\{ 1 + \frac{S^2 \exp[-V(S)/kT]}{\tilde{S}(\pi Dt)^{1/2}} \right\} \quad (2.114)$$

where the steady-state transport rate

$$\alpha_{tr} = 4\pi \tilde{S} D = 4\pi D R_e / P(S) \equiv \alpha_{hl} \quad (2.115)$$

with

$$P(S) = R_e / \tilde{S} = R_e \int_S^\infty \exp(V/kT) \frac{dR}{R^2}, \quad (2.116)$$

in terms of the natural length e^2/kT as in (2.56). Under the condition of equilibrium with the field when the Einstein relation written as $DR_e = K\epsilon$ holds, the steady-state solution is, for a coulombic attraction

$$\alpha_{hl}^{(s)} = 4\pi K\epsilon / [1 - \exp(-R_e/S)], \quad (2.117)$$

as previously obtained by Bates (1975) via the steady-state analysis of an instantaneous sink, leading to (2.73). The present paper represents the first time, to the author's knowledge, that the transient solutions (2.113) and (2.114) for instantaneous reaction in the presence of a general field have been obtained. Since constant $(d\tilde{R}/d\tilde{\tau})$ is assumed in (2.111b), $(\tilde{R} - \tilde{S})(d\tilde{R}/d\tilde{\tau})$ can be replaced by $R - S$ which yields a result also obtained via (2.111c).

The boundary condition (2.91b) for finite reaction under a field is

$$\Gamma_3(S) n^-(S, t) = D \exp[-V(S)/kT] \{ \partial [n(R, t) \exp(-V/kT)] / \partial R \}, \quad (2.118)$$

which for (2.111b) and (2.111c) transforms as

$$\left[\frac{\partial n'}{\partial \tilde{r}} \right]_0 = \left(\frac{\alpha_{rn}}{\alpha} \right) n'(0, t) \quad (2.119a)$$

and

$$\left[\frac{\partial n'}{\partial r} \right]_0 = \left(\frac{\alpha_{rn}}{\alpha} \right) \left(\frac{d\tilde{r}}{dr} \right)_0 n'(0, t) = \left(\frac{\alpha_{rn}}{\alpha} \right) \left[\frac{\tilde{S}}{S} \exp V(S)/kT \right] n'(0, t) \quad (2.119b)$$

respectively, where

$$\alpha_{rn} = 4\pi S^2 \Gamma_3 \exp(-V(S)/kT), \quad \alpha = (\alpha_{rn} \alpha_{tr}) / (\alpha_{rn} + \alpha_{tr}) \quad (2.120)$$

are the reaction and recombination rates, as before.

Hence, after exercising due care, we obtain for a general interaction the full time-dependent solution obtained from Laplace transformation of (2.111b) subject to boundary conditions (2.90) and (2.119a), and to the Boltzmann initial condition (2.92):

$$n(R, t) = N^- \exp(-V/kT) \{ 1 + (\alpha/\alpha_{tr}) (\tilde{S}/\tilde{R}) [\exp(2\tilde{\Omega}\tilde{\chi}) \exp \tilde{\chi}^3 \operatorname{erfc}(\tilde{\chi} + \tilde{\Omega}) - \operatorname{erfc} \tilde{\Omega}] \}, \quad (2.121a)$$

where

$$\tilde{\chi}(t) = (1 + \alpha_{rn}/\alpha_{tr}) (\tilde{D}t)^{1/2} / \tilde{S}, \quad (2.121b)$$

$$\tilde{\Omega}(t) = (\tilde{R} - \tilde{S}) / 2(\tilde{D}t)^{1/2}, \quad (2.121c)$$

in terms of (2.105) and (2.109). Solution of (2.111c) subject to (2.119b) also yields (2.121a) but with \tilde{D} evaluated at S , and with $\tilde{\Omega}$ replaced by Ω of (2.102), which are essentially equivalent since constant $d\tilde{R}/dR$ is basic to both methods.

The full time-dependent recombination rate now follows from (2.121a) as

$$\alpha(t) = \alpha_3 n^-(S, t) / N^- = \alpha [1 + (\alpha_{rn}/\alpha_{tr}) \exp \tilde{\chi}_S^3 \operatorname{erfc} \tilde{\chi}_S], \quad (2.122a)$$

where $\tilde{\Omega}(R=S)$ in (2.121c) vanishes, $\tilde{\chi}$ in (2.121b) is, with the aid of (2.105), (2.109) and (2.121),

$$\tilde{\chi}_S = \left(1 + \frac{\alpha_{rn}}{\alpha_{tr}} \right) \frac{(Dt)^{1/2}}{S} \exp[V(S)/kT] \left[S \int_S^\infty \exp(V/kT) R^{-3} dR \right]^{-1}, \quad (2.122b)$$

at S . For the field-free case ($V=0$), (2.121) and (2.122) reduce to the diffusion-controlled results (2.100) and (2.104), respectively. Expressions (2.120) and (2.122) are the analytical time-dependent densities and rates obtained from (2.89) for an arbitrary spherical field $V(R)$ for an initial Boltzmann distribution, and are accurate where $(d\tilde{r}/dr)$ can be assumed constant in (2.111a).

As t increases from zero,

$$\exp \chi^3 \operatorname{erfc} \chi \rightarrow 1 - (2/\sqrt{\pi}) \chi + \chi^2 - (4/3\sqrt{\pi}) \chi^3 + \dots \quad (2.123)$$

such that

$$\alpha(t \rightarrow 0) = \alpha_{rn} \left\{ 1 - \frac{2}{\sqrt{\pi}} \frac{\alpha_{rn}}{\alpha_{tr}} \frac{(Dt)^{1/2}}{S} \exp[V(S)/kT] \left[S \int_S^\infty \exp(V/kT) R^{-3} dR \right]^{-1} \right\} \quad (2.124)$$

decreases initially from the reaction rate α_{rn} . As $t \rightarrow \infty$,

$$\exp \chi^3 \operatorname{erfc} \chi \rightarrow (1/\chi\sqrt{\pi}) (1 - 1/2\chi^2 + 3/4\chi^4 \dots), \quad (2.125)$$

such that the long-time dependence is

$$\alpha(t \rightarrow \infty) = \alpha \left\{ 1 + \frac{\alpha}{\alpha_{tr}} \frac{S \exp[-V(S)/kT]}{(\pi Dt)^{1/2}} \left[S \int_S^\infty \exp(V/kT) R^{-3} dR \right] \right\}. \quad (2.126)$$

The transient rates (2.124) and (2.126) for short and long intervals of time are best observed at high gas densities when $\alpha_{rn} \gg \alpha_{tr} \approx \alpha$ respectively. The full transient densities (2.121) and rates (2.122) are of basic significance to all diffusion-drift phenomena in gases or dilute solutions, such as ion-ion, ion-atom and atom-atom recombination in dense gases, or coagulation of colloids in ionic solutions.

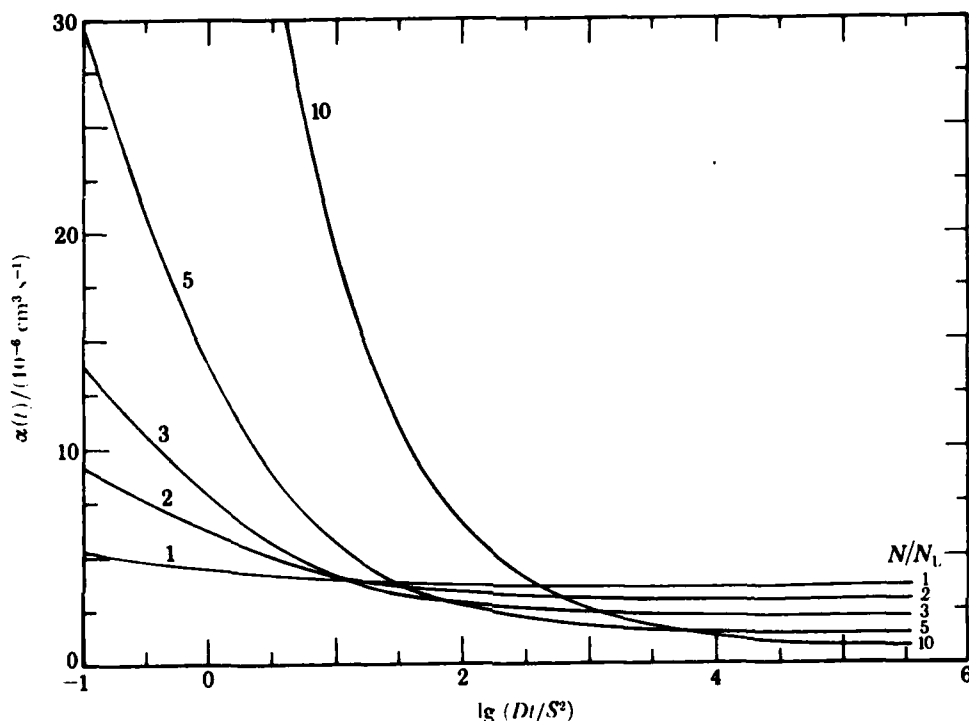


FIGURE 1. Explicit time dependence of recombination rate $\alpha(t)$ at various gas densities N (in multiples of the Loschmidts number $N_L = 2.69 \times 10^{19} \text{ cm}^{-3}$ at s.t.p.). Characteristic times (S^2/D) for diffusion are (16, 11, 8, 5, 3) $\times 10^{-12} \text{ s}$ for $N/N_L = 1, 2, 3, 5, 10$ respectively.

The full time dependence in (2.122a) for α is contained in (2.122b) for χ_S which, for a pure coulomb attraction, varies as

$$\tilde{\chi}_S(\tau) = (1 + \alpha_{rn}/\alpha_{tr}) \tau^{\frac{1}{2}} (R_e/S) [\exp(R_e/S) - 1]^{-1}, \quad (2.127)$$

where the scaled time is

$$\tau = t/(S^2/D) \quad (2.128)$$

where S^2/D is the approximate time required for an ion to diffuse from the boundary to the centre of the sink.

With the aid of a simple expression, (4.12a), and associated quantities, derived in § 4.2 for the reaction rate α_{rn} , and the exact expression (2.63) or (2.71) for the transport rate, the full time dependence of the recombination rate (2.122a) can be explored. Figure 1 illustrates the variation of $\alpha(t)$ with t for several values (1, 2, 3, 5, and 10) of the gas density N (in multiples of $N_L = 2.69 \times 10^{19} \text{ cm}^{-3}$, the number density at s.t.p.). These rates are appropriate to a fictitious (but representative) case of equal masses ($M = 16 \text{ a.m.u.}$) of the ionic species with mobility $2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in an equal-mass gas and with δ_1 in (4.17) taken as 0.6 (Flannery 1978). Figure 1 exposes features of basic significance to the physics of recombination.

Since the initial ion distribution is assumed to be in Boltzmann equilibrium, the initial rate of

recombination $\alpha(t = 0)$ is simply the reaction rate α_{rn} , in accord with (2.124). The ions then begin their transport and replace the reacted ions within a time S^2/D . Since the recombination is determined by the rate-limiting step of reaction and transport, its variation with time is best observed at high gas densities N where $\alpha_{rn} \gg \alpha_{tr}$ such that α decreases from α_{rn} to α_{tr} , the steady-state limit at $t \gg S^2/D$. Variation of α with t for $N \approx 10N_L$, for example, reflects the change in α from reaction controlled transport. The reaction rate at high N ($\gtrsim 5N_L$) is so large because the radial extent S of the sink becomes so contracted that the Boltzmann distribution of ions at its boundary is locally very large and offsets the inherent reduction in cross section. For $N \approx N_L$ and lower, the transport is always faster than the reaction such that the reaction rate limits the rate of recombination at all times, and a straight-line dependence is observed as in figure 1. The steady-state limit is, of course, independent of any initial condition adopted.

Measurement of the variation of α with t at high N ($\gtrsim N_L$) would, therefore provide valuable information about the physics intrinsic to recombination, i.e. of the transport component at $t \gg S^2/D$ and, more significantly, of the reaction component at high densities when $t \lesssim S^2/D$. Such experiments are feasible with modern techniques such as laser spectroscopy. In figure 1 are indicated relevant time-scales. The radii S of the sinks are compressible (§ 4.2) as N is raised, and the unit of time (S^2/D) varies from 1.6×10^{-11} s at a gas pressure of about 1 atm to 3×10^{-12} s at ca. 10 atm. The laser can be tuned to some known molecular rotational or vibrational transition since electronic transitions are precluded because of the time-scale. The ion densities can then be determined by fluorescence.

Figure 1 is, therefore, a striking illustration of the transition in recombination from reaction alone to the limiting step of reaction or transport. Verification is feasible, not only by laboratory experiment but also by Monte-Carlo computer experiments such as those of Bates (1980c) and of Bardsley & Wadehra (1980), suitably generalized to include explicit time dependence.

The basic equation (2.89) can be written to incorporate both the condition (2.91b) for a finite rate α_{rn} of reaction and the possibility of a scavenger reaction proceeding in parallel at a rate γn , by

$$-\frac{\partial n}{\partial t} + \nabla \cdot \mathbf{j} - \gamma n = \Gamma_3 n \delta(R - S). \quad (2.129)$$

By Laplace transformation, we can show that the time-dependent solutions are given by $n \exp(-\gamma t)$ and $\alpha \exp(-\gamma t)$, with n and α given by (2.121a) and (2.122a), respectively.

Finally, transient solutions of (2.129) appropriate to other initial conditions are important, for example where intense ionization is deposited into or produced within a localized system either by a high energy beam of particles or by radiation such that many ions may diffuse out of the localized system before neutralization occurs. The rate of disappearance of ion-ion or electron-ion pairs scattered along the track of the ionization beam is time-dependent and is given by the appropriate solution of (2.129) applicable to 'columnar' recombination rather than 'volume' recombination as discussed here.

When \mathcal{N} ions are generated instantaneously by a spherical surface source at distance R_0 from the central positive ion, i.e. R_0 -ion pairs are produced, (2.89) is solved subject to

$$\left. \begin{aligned} n(R, t = 0) &= \mathcal{N} \exp(-V/kT) \delta(R - R_0) / 4\pi R_0^2, \\ j(S, t) &= \Gamma_3 n(S, t), \\ n(R \rightarrow \infty, t) &= 0. \end{aligned} \right\} \quad (2.130)$$

For the field-free case ($V = 0$), by analogy with the corresponding problem in heat conduction (Carslaw & Yeager 1959), the solution can be written in terms of the quantities χ and Ω associated with a continuous source at infinity as

$$n(R, t; R_0, S) = \frac{\mathcal{N}}{4\pi R R_0} \frac{1}{(4Dt)^{1/2}} \left\{ \frac{1}{\sqrt{\pi}} [\exp(-\Omega_0^2) + \exp(-\Omega_1^2)] - 2\chi \exp \chi^2 \exp 2\Omega_1 \chi \operatorname{erfc}(\chi + \Omega_1) \right\}, \quad (2.131)$$

$$\text{where} \quad \Omega_0 = (R - R_0)/2(Dt)^{1/2}, \quad \Omega_1 = (R + R_0 - 2S)/2(Dt)^{1/2} \quad (2.132)$$

$$\text{are similar to (2.102), and} \quad \chi(t) = (1 + \alpha_3/\alpha_d)(Dt)^{1/2}/S, \quad (2.133)$$

as before (equation (2.101)) in terms of (2.91c) and (2.99). If the ions are generated at the reaction surface, $R_0 = S$ and $\Omega_0 = \Omega_1$. The volume external to the spherical surface of the sink is \mathcal{V} so that the frequency (s^{-1}) of recombination is then

$$\begin{aligned} \nu_r(t) &= - \int_{\mathcal{V}} \left(\frac{\partial n}{\partial t} \right) dR = 4\pi S^2 \Gamma_3 n(S, t; R_0 = S) \\ &= [\mathcal{N} \Gamma_3 / (4Dt)^{1/2}] [2/\sqrt{\pi} - 2\chi(t) \exp \chi^2 \operatorname{erfc} \chi] \\ &\equiv - [\mathcal{N} \Gamma_3 / (4Dt)^{1/2}] d(\exp \chi^2 \operatorname{erfc} \chi) / d\chi \end{aligned} \quad (2.134)$$

The initial frequency $\nu_r(0)$ is $\mathcal{N} \Gamma_3 / (\pi Dt)^{1/2}$, and as $t \rightarrow \infty$, $\nu_r \rightarrow$ zero as $\nu_r(0)/2\chi^2$. The total number of ions that have recombined after time t is

$$\mathcal{N}_r(t) = \int_0^t \nu_r(t) dt = \mathcal{P}_r \mathcal{N} [1 - \exp \chi^2(t) \operatorname{erfc} \chi(t)] \rightarrow \begin{cases} (2/\sqrt{\pi}) \mathcal{P}_r \mathcal{N} \chi, & t \rightarrow 0, \\ \mathcal{P}_r \mathcal{N}, & t \rightarrow \infty, \end{cases} \quad (2.135)$$

where the probability of recombination in the absence of the field V is

$$\mathcal{P}_r(V \rightarrow 0) = \alpha_3 / (\alpha_3 + \alpha_d) \quad (2.136)$$

and remains less than unity in the presence of outward diffusion.

For a general field $V(R)$, the general solution appropriate to (2.130) is obtained by use of transformation (2.105) and of (2.111c) to yield.

$$\begin{aligned} n(R, t; R_0, S) &= \frac{\mathcal{N} \exp(-V/kT)}{4\pi R_0^2} \left(\frac{R_0}{R} \right) (4Dt)^{-1/2} \left\{ \frac{1}{\sqrt{\pi}} [\exp(-\Omega_0^2) \right. \\ &\quad \left. + \exp(-\Omega_1^2)] - 2\tilde{\chi}_S \exp \tilde{\chi}_S^2 \exp 2\Omega_1 \tilde{\chi}_S \operatorname{erfc}(\tilde{\chi}_S + \Omega_1) \right\}, \end{aligned} \quad (2.137)$$

in terms of the corresponding tilde quantities (2.105) and (2.122b). For a coincident source and sink, the recombination frequency is

$$\nu_r(t) = [\mathcal{N} \Gamma_3 / (4Dt)^{1/2}] [2/\sqrt{\pi} - 2\tilde{\chi}_S(t) \exp \tilde{\chi}_S^2 \operatorname{erfc} \tilde{\chi}_S] \exp(-V(S)/kT), \quad (2.138)$$

where $\tilde{\chi}_S$ is given by (2.122b). The number of recombined pairs after time t is

$$\mathcal{N}_r(t) = \mathcal{P}_r \mathcal{N} [1 - \exp \tilde{\chi}_S^2 \operatorname{erfc} \tilde{\chi}_S], \quad (2.139)$$

where the probability of recombination in the presence of general V , in terms of the reaction and transport rates α_{rn} and α_{tr} , respectively, is

$$\mathcal{P}_r = \alpha_{rn} / (\alpha_{tr} + \alpha_{rn}), \quad (2.140)$$

as before (equation (2.77d)). Thus \mathcal{P}_r is controlled by the relative rates of reaction and transport. At low N , $\mathcal{P}_r \rightarrow \alpha_{rn}/\alpha_{tr}$ while at high N , $\mathcal{P}_r \rightarrow 1$. Expressions (2.121a), (2.122a), (2.137) and

(2.138) represent the first time that analytical solutions of the Debye-Smoluchowski equation subject to conditions (2.90)–(2.92) and (2.130), respectively, have been developed for any (general) interaction $V(R)$.

The above analysis has therefore shown that the same key quantities appear in two distinct time-dependent problems: homogeneous recombination where the process is driven by a source operating continuously at infinity; and geminate recombination where the process is initially established by an instantaneous source of ion pairs within the medium (as produced by a laser burst) and is controlled by the relative reaction and transport rates.

For intense ionization, the interaction between the ions can no longer be assumed *ab-initio* to be pure coulomb. The interaction V must then be determined by self-consistent (with the recombination) methods as developed in §4.

Competition between the increased number of sinks (assumed equivalent) for the flux incident from infinity is acknowledged by the last term of the following equation:

$$\partial \rho(R, t) / \partial t = \nabla \cdot \mathcal{J}_1 \rho - \Gamma_3 \rho \delta(R - S) - \alpha(t) \langle \rho(t) \rangle_S \rho(R, t), R \geq S, \quad (2.141)$$

for the concentration ρ in cm^{-3} of R -ion pairs such that ρdR is the concentration of ion pairs with internal separation R in the interval dR about R . In (2.141) the density of unreacted ion pairs (with $R > S$) is

$$\langle \rho(t) \rangle_S = \int_S^\infty \rho(R, t) dR = \int_S^\infty 4\pi R^2 \rho(R, t) dR, \quad (2.142)$$

and the inward diffusional-drift operator \mathcal{J}_1 is given by (2.45) since we assume in addition that the diffusion coefficient D remains constant. Substitute

$$\rho(R, t) = C(t) g(R, t) \quad (2.143)$$

in (2.141) where C satisfies

$$\partial C(t) / \partial t = -\alpha \langle g(t) \rangle_S C^2(t), \quad (2.144)$$

such that the probability density or pair correlation function $g(R, t)$ satisfies the usual Debye-Smoluchowski equation,

$$\partial g / \partial t = \nabla \cdot \mathcal{J}_1 g - \Gamma_3 g \delta(R - S) \quad (2.145)$$

for an isolated sink surrounding a positive ion (say).

Thus

$$C(t) = C_0 \left/ \left[1 + C_0 \int_0^t \alpha(t) \langle g(t) \rangle_S dt \right] \right., \quad (2.146)$$

where C_0 is the initial concentration of ion pairs, describes the time decay of all ion pairs via recombination, and $g(R, t)$ describes the spatial distribution of R -ion pairs. The recombination rate

$$\alpha(t) = -\frac{d}{dt} \left[\int_S^\infty 4\pi R^2 \rho(R, t) dR \right] / N^+ N^-, \quad (2.147)$$

therefore satisfies

$$\alpha(t) \{ 1 - (\langle g(t) \rangle_S^2 C^2(t) / N^+ N^-) \} = \alpha_0(t) C(t) / N^+ \quad (2.148)$$

where α_0 is the rate that is obtained from appropriate solution of (2.145) for an isolated sink (or constant C). When the initial concentration C_0 and the recombination time t are sufficiently small that

$$C_0 \int_0^t \alpha(t) \langle g(t) \rangle_S dt \ll 1, \quad (2.149)$$

and $C(t)$ remains constant $\approx N^\pm$ then equations (2.147) and (2.148) reduce to the case of an isolated sink with associated rate α_0 .

3. 'GENERALIZED QUASI-EQUILIBRIUM', STEADY-STATE METHOD FOR THE REACTION AND TRANSPORT RATES

Rather than from the complete determination of α via solutions of (2.20) inserted in (2.52), or alternatively in (2.59) via α_3 of (2.44), intrinsic physics may yet be uncovered from the solution of (2.43) with (2.44) modified by a procedure suggested by (2.35): either neglect upward transitions k_{II} ; or, in effect, rewrite the energy-change frequency terms on the right-hand side of (2.47a), with the aid of the null-collision relation (2.41), as

$$N \sum_{I=-E}^E \left(N_I^* \sum_{I'=-V}^E k_{II'} - \sum_{I'=-M}^E N_I^* k_{II'} \right) \approx N^* \nu(R), \quad (3.1)$$

where $\nu(R)$ is some averaged collision frequency v_d/λ in terms of a mean free path λ . With the aid of (2.46), (2.53) and of relation (2.10), (2.50) in this approximation yields,

$$4\pi R^2 D \left[\frac{dn(R)}{dR} + n(R) \frac{d(V/kT_{eff})}{dR} \right] = \alpha_3(R) n(R) \approx 4\pi \int_0^{\min(R, R_E)} \nu(R) n(R) R^2 dR, \quad (3.2a)$$

$$= \begin{cases} \sim \frac{4\pi}{\lambda} D R^2 n(R), & R \leq R_E, \\ F_c(R_E), \text{ a constant,} & R \geq R_E, \end{cases} \quad (3.2b)$$

$$(3.2c)$$

in which the speed v_d used for ion pairs within the collisional sink that extends to R_E is assumed to be mainly controlled by the speed D/R (cf. Flannery 1976) of *inward* diffusion due to the effect of the sink on the ion distribution. By use of an integrating factor $\exp(V/kT - R/\lambda)$, (3.2b) is solved to yield

$$n(R) \exp(V/kT) \exp(-R/\lambda) = n(R_E) \exp[V(R_E)/kT] \exp(-R_E/\lambda) \quad (3.3)$$

for $R \leq R_E$. For $R \geq R_E$ when the sink exerts a constant effect, the right-hand side of (3.2c) is constant so that the constant flux solution (2.58a) applies. Hence, continuity at R_E requires

$$n(R) \{ \exp[V(R)/kT] \exp(R_E - R)/\lambda + [P(R_E)/\alpha_h] \alpha_3(R) \} = N^-, \quad R \leq R_E, \quad (3.4)$$

where the constant flux F_c in (3.2c) is equivalent to $\alpha_3(R) n(R)$ for $R \geq R_E$. The overall recombination coefficient is,

$$\alpha = \frac{1}{N^-} [\alpha_3(R_E) n(R_E)] = \frac{\{\alpha_3(R_E) \exp[-V(R_E)/kT]\} \alpha_h / P(R_E)}{\alpha_3(R_E) \exp[-V(R_E)/kT] + \alpha_h / P(R_E)} \quad (3.5)$$

as before. Since α_h varies as N^{-1} , at low densities (and for small R), when the second term in the right-hand side of (3.4) can be neglected in comparison with the first,

$$\begin{aligned} n(R) &= N^- \exp[-V(R)/kT] \exp(R - R_E)/\lambda, \quad R \leq R_E \\ &= n_0(R) \exp(R - R_E)/\lambda. \end{aligned} \quad (3.6)$$

Hence (3.2a) yields

$$\alpha_3(R_E) n_0(R_E) = \frac{4\pi}{\lambda} N^- \exp(-R_E/\lambda) \int_0^{R_E} v_d \exp[-V(R)/kT] \exp(R/\lambda) R^2 dR. \quad (3.7)$$

The speed $v_d \exp(-V/kT)$ appropriate to the distribution (3.6) is taken as approximately its thermal value $\langle v \rangle$ corresponding to energies greater than $-E$. Hence, at low densities,

$$\alpha_3(R_E) \exp[-V(R_E)/kT] = (4\pi \langle v \rangle / \lambda^2) \{ [2 - 2(R_E/\lambda) + (R_E/\lambda)^2] - 2 \exp(-R_E/\lambda) \} \quad (3.8)$$

which, in the low density limit, reduces to

$$\alpha_3(R_E) \exp[-V(R_E)/kT] = \frac{4\pi R_E^3 \langle v \rangle}{3\lambda} \left[1 - \frac{1}{2}(R_E/\lambda) + \frac{1}{20}(R_E/\lambda)^2 - \frac{1}{120}(R_E/\lambda)^3 + \dots \right], \quad (3.9)$$

which exhibits an N -variation ($\lambda \sim N^{-1}$) similar to the low density limit of the expression of Thomson (1924). At low densities $\alpha_n \gg \alpha_3$, so that the actual recombination coefficient is

$$\alpha \xrightarrow{\text{low } N} \alpha_3(R_E) \exp[-V(R_E)/kT] \equiv \alpha_{rn}, \quad (3.10)$$

the reaction rate.

At high gas densities $\alpha_3 \gg \alpha_n$ such that the actual recombination coefficient (3.5) approaches the limit,

$$\alpha \xrightarrow{\text{high } N} \alpha_n/P(R) \equiv \alpha_{tr} \quad (3.11)$$

the transport rate. Hence, this procedure has shown again that

$$\alpha = \alpha_{rn} \alpha_{tr} / (\alpha_{rn} + \alpha_{tr}) \quad (3.12)$$

is limited by either the transport or the reaction rates whose variation with N is contained in (3.9)–(3.11).

The above simplified model, designed to reproduce the result of a detailed history of energy changes in ion pairs via ion-neutral collisions in a dense gas (which can be established) suggests introduction of phenomenological ion and ion-pair densities

$$\tilde{n}(R) = n(R) \exp(s/\lambda), \quad \tilde{N}(R) = N(R) \exp(s/\lambda), \quad (3.13)$$

where s is the radial length $R_E - R$ from some radius R_E within which energy-changing collisions are effective.† Hence, (3.2b) with T_{eff} replaced by T yields,

$$\frac{d\tilde{n}(R)}{dR} + \tilde{n}(R) \frac{\partial(V/kT)}{\partial R} = 0, \quad (3.14)$$

which can be solved to yield,

$$n(R) = N \exp(-V/kT) \exp(-s/\lambda) \equiv \sum_{i=-\infty}^{\infty} n_i(R, E_i), \quad R \leq R_E, \quad (3.15)$$

where $n_i(R, E_i)$ satisfies the system of equations (2.20) that describe microscopic events. When the effect of the sink operating in the $(-M \rightarrow -V)$ range of energy levels is small, the right-hand side of (2.20) can be taken as approximately zero such that solution of the left-hand side set to zero yields the Maxwell-Boltzmann distribution $n_0(R, E_i)$ in (2.14) for ions in thermodynamic equilibrium. When n_0 is summed over all E_i , or integrated over all v_i as in (2.9) the Boltzmann term in (3.15) is obtained. Provided that the effect of the sink is small for ion pairs with internal energy greater than $-E$, an iterative solution can be proposed by assuming the left-hand side of (2.20) to be zero, as if in full equilibrium, and then including the sink to first order by solving the equation

$$\int_0^R dR N_i^*(R, E_i) \sum_{t=-\infty}^{\infty} k_{it}(R) = \int_0^R dR \sum_{t=-M(R)}^{\infty} N_t^*(R, E_t) k_{ti}(R), \quad (3.16)$$

which follows from (2.20). Since the E_i - or v_i -averaged effect of the left-hand side of (2.20) is measured by $\mathcal{L}n(R)$ on the left-hand side of (2.47) and hence, in the approximation (3.2a) basic

† In this sense Thomson (1924) displayed remarkable intuition in his concept of a trapping radius, a concept fully exploited in §2.4, §2.5 and §4.2 in the form of sinks compressible with N .

to this section, by \tilde{n} of (3.13), the small departures of the left-hand side of (2.20) from zero can be reintroduced by replacing N_1^* in (3.16) by the fictitious densities

$$\tilde{N}_1(R, E_1) = N_1^*(R, E_1) \exp(s/\lambda). \quad (3.17)$$

Provided the level $-E$ is sufficiently high that departures from thermodynamic equilibrium are indeed small, and yet is sufficiently low in the bound spectrum that $v_1(R)$ on the left-hand side of (2.20) does not depart appreciably from zero, its value at the turning points, it follows that densities of bound ion-pairs with $E_1 < -E$ can still be obtained from (3.16); and replacement of N_1^* by \tilde{N}_1 will minimize any error in the original assumption.

The recombination coefficient α_3 associated with negative ion density $n(R)$ is therefore, in this approximation,

$$\alpha_3(R_E) = \frac{N}{N^+N^-} \int_0^{R_E} \exp(-s/\lambda) dR \sum_{i=-E}^C \left[\tilde{N}_i(R, E_i) \sum_{t=-\infty}^{-E} k_{it}(R) - \sum_{t=-M(R)}^C \tilde{N}_t(R, E_t) k_{ti}(R) \right], \quad (3.18)$$

and the overall recombination coefficient appropriate to the R -asymptotic density N^- can then be obtained from (2.52) directly or from (2.59).

In the limit of low gas densities N , and low ion densities N^\pm , departures from thermodynamic equilibrium are indeed small, $\alpha \rightarrow \alpha_3$ and $\lambda \rightarrow \infty$ such that (3.18), on reordering integrations, can be rewritten as,

$$\alpha_3(-E) = \frac{N}{N^+N^-} \sum_{i=-E}^C \left[\sum_{t=-D}^{-E} \int_0^{R_m} N_i^*(R, E_i) k_{it}(R) dR - \sum_{t=-S}^{-E} \int_0^{R_m} N_t^*(R, E_t) k_{ti}(R) dR \right], \quad (3.19)$$

where $-D$ is the lowest bound level of the system, $-S$ is the stabilization level of energy $-E_s$, and $R_m = \min[R(E_1), R(E_t)]$, the minimum of the outermost turning points associated with levels E_1 (bound and continuous) and E_t (bound) respectively. Since $(0 \rightarrow R_m)$ defines the full range accessible classically, i.e.

$$N_i(E_1) \langle k_{it}(E_1, E_t) \rangle = \int_0^{R_m} N_i^*(R, E_i) k_{it}(R; E_1, E_t) dR, \quad (3.20)$$

for k_{it} given previously (Flannery 1980, 1981a) we have

$$\alpha \xrightarrow{\text{low } N} \alpha_3(-E) = \frac{N}{N^+N^-} \sum_{i=-E}^C \left[N_i(E_1) \sum_{t=-D}^{-E} \langle k_{ti} \rangle - \sum_{t=-S}^{-E} N_t(E_t) \langle k_{ti} \rangle \right], \quad (3.21)$$

where the ion-pair number density in the classical accessible region is,

$$N_i(E_1) = \int_0^{R(E_1)} N_i^*(R, E_i) dR \quad (3.22)$$

which, with the aid of (3.16) with integrations reordered, and of (3.20), satisfies

$$N_i(E_1) \sum_{t=-D}^C \langle k_{it} \rangle = \sum_{t=-S}^C N_t(E_t) \langle k_{ti} \rangle. \quad (3.23)$$

Equations (3.21) and (3.23) are identical with those originally introduced by Bates & Moffett (1966) and by Bates & Flannery (1968) in their effectively exact quasi-equilibrium treatment of the low density limit of ion-ion recombination. Because of this, and of the constant flux assumption implicit in (3.2c), the method represented by (3.16)–(3.18) and (2.59) is designated as the 'generalized-quasi-equilibrium-distribution' steady-state method to remind us of the underlying assumptions.

4. THEORY OF ION-ION RECOMBINATION AS A FUNCTION OF ION DENSITY

All previous theoretical and experimental studies of ion-ion recombination pertain to a dilute degree of ionization with ion densities $N^\pm \sim 10^8 \text{ cm}^{-3}$ for which a coulombic ion-ion interaction is correct. Ion-ion recombination plays a key role (Flannery 1979) in populating the upper laser electronic levels of rare gas-halide systems which operate not only at high gas pressure ($\frac{1}{2}$ –10 atm) but also at relatively high ion densities $10^{12} \lesssim N^\pm \lesssim 10^{14} \text{ cm}^{-3}$. In § 4.1 is developed a theory for the variation of α with N^\pm . A useful procedure proposed in § 4.2 for the rapid evaluation of the reaction rate α_{rn} permits illustration of the variation of α with gas density N .

4.1. General theory

The interaction V between the positive and negative ions can no longer be assumed, *ab initio*, to be pure coulomb, but depends on the increased screening due to the other ions via their net charge-density distribution which, in turn, is coupled self-consistently to the recombination sink via α which contains an explicit dependence on V . Repulsion between like ions also becomes important. The interaction V between the ions is determined by appropriate solution of Poisson's equation

$$\nabla^2 V(R) = (4\pi e^2/\epsilon) [n^+(R) - n^-(R)], \quad (4.1)$$

where the local positive and negative ion densities are $n^\pm(R)$, and ϵ is the dielectric constant $1 + 4\pi Np$ of a gas with polarizability p and density N . For Xe, $\epsilon = (1 + 1.4 \cdot 10^{-3} N/N_L)$, in effect unity for $N \lesssim 25(N_L)$, the number density ($2.69 \times 10^{19} \text{ cm}^{-3}$) at s.t.p.). In the steady-state limit when few unreacted ions are within the recombination sink measured by R_E of § 2, the net inward flux (in s^{-1}) of positive ions towards the central positive ion is

$$F_{in}^{++}(R) = -4\pi R^2 \left[-D^+ \frac{dn^+(R)}{dR} + n^+(R) \frac{K^+ \partial V}{\epsilon \partial R} \right], \quad (4.2)$$

where D^+ and K^+ are the relative quantities $2D_1$ and $2K_1$ in terms of the diffusion coefficient D_1 and mobility K_1 for a positive ion 1. The net inward flux of negative ions 2 towards a positive ion 1 is,

$$F_{in}^{-+}(R) = 4\pi R^2 \left[D \frac{dn^-(R)}{dR} + n^-(R) \frac{K \partial V}{\epsilon \partial R} \right], \quad (4.3)$$

where D and K are the relative diffusion coefficients ($D_1 + D_2$) and relative mobilities ($K_1 + K_2$) for ions 1 and 2. In the reference frame of the central positive ions, assumed stationary, F_{in}^{++} vanishes, and integration of (4.2) yields the Boltzmann distribution

$$n^+(R) = N^+ \exp[V(R)/kT], \quad (4.4)$$

where T is given by T_{eff} in (2.57) when the Einstein relation no longer holds. Hence, Poisson's equation for spherical distributions is

$$\frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial V}{\partial R} \right) = \left(\frac{4\pi e^2}{\epsilon} \right) \{ N^+ \exp[V(R)/kT] - n^-(R) \}. \quad (4.5)$$

For a single isolated sink, the steady-state density $n^-(R)$ of negative ions is given by (2.64), and

$$\frac{1}{R^2} \frac{\partial}{\partial R} \left[R^2 \frac{\partial (V/kT)}{\partial R} \right] = \frac{1}{2R_0^2} \left\{ \exp[V(R)/kT] - \left[1 - \frac{\alpha}{\alpha_{tr}} \frac{P(R)}{P(R_E)} \right] \exp[-V(R)/kT] \right\}, \quad (4.6)$$

where the 'screening' distance is

$$R_0 = (8\pi N^\pm R_E/\epsilon)^{-1/2}. \quad (4.7)$$

The R -variation of the right-hand side of (4.6) is given explicitly by $V(R)$ and $P(R)$ and the interaction is contained implicitly within the recombination probability,

$$\alpha/\alpha_{tr} = \alpha_{rn}(R_E)/[\alpha_{rn}(R_E) + \alpha_{tr}(R_E)], \quad (4.8)$$

from (2.62), where α_{rn} is the reaction rate (2.61), i.e. the recombination coefficient that would pertain provided a Boltzmann distribution of ions (with no net transport) were maintained as at low gas densities N , and α_{tr} is the transport rate (2.63), i.e. the recombination coefficient that pertains for instantaneous reaction within R_E , as at high N . If an analytic expression for α_{tr} is known in terms of V , as in §4.2, then a self consistent V can be obtained from (4.6) with (4.8), since α_{tr} is given in terms of V by the analytical expression (2.63). Otherwise, (4.5) must be coupled to the solution of

$$\begin{aligned} 4\pi R^2 \left[D \frac{dn^-(R)}{dR} + n^-(R) \frac{K \partial V}{\partial R} \right] &\equiv 4\pi R^2 D \left\{ \exp(-V/kT) \frac{d}{dR} [n^-(R) \exp(V/kT)] \right\} \\ &= \alpha_3(R) n^-(R) = \alpha N^- \end{aligned} \quad (4.9)$$

for $n^-(R)$, where the right-hand side of (4.9) is given by (2.50) in terms of the phase-space densities $n_1(R, E_1)$ determined from (2.20) with collisional rates $k_{tr}(R)$, which in turn depend on V .

Hence the general theory involves the coupled solutions of the Poisson equation (4.5), of the flux equation (4.9), and of the Boltzmann equation (2.20), i.e. the interaction V is solved self-consistently with the recombination. Application of this general theory represents a formidable but yet a feasible task with the aid of new theoretical procedures for the solution of (2.20) for the phase-space densities $n_1(R, E_1)$.

Note that it is only $\alpha_3(R)$ that depends on explicit knowledge of $n_1(R, E_1)$ so that, provided the rate α_{rn} of reaction can be provided analytically by alternative procedures, the above prescription reduces to the solution of (4.6) with (4.8). The term $1 - (\alpha/\alpha_{tr}) [P(R)/P(R_E)]$, which depends on V , N and R , on the right-hand side of (4.6), tends to unity at low N for all R , and increases at high N , from zero at $R \sim R_E$ to unity as $R \rightarrow \infty$. As $R_E \rightarrow \infty$ for no plasma sheathing, solution of (4.6) is pure coulomb so that a (first) iterative solution valid for low N^\pm (large R_E) and high N in the vicinity of R_E is

$$\frac{V_h(R)}{kT} = -\frac{R_e}{R} + \frac{1}{12} \left(\frac{R}{R_E} \right)^2 \exp(-R_e/R_E), \quad R_E \lesssim R \ll R_s, \quad (4.10)$$

where R_e is the natural unit (e^2/kT) of length. High-order iterations may be obtained. This interaction (4.10) is pure coulomb for $R \ll R_e$ as at high N , or else, for $R^3 \ll 12R_e R_E^2$, i.e. when $N^\pm \lesssim 10^{14} \text{ cm}^{-3}$ at $R \lesssim R_e$.

To facilitate numerical solution, equation (4.6) may be decomposed into three coupled first-order differential equations,

$$\left. \begin{aligned} dv_1/dr &= v_2(r), \\ dv_2/dr &= -(2/r) v_2(r) + (1/2r^2) [\exp v_1(r) - v_3(r) \exp -v_1(r)], \\ dv_3/dr &= (\alpha/\alpha_h) \exp v_1(r)/r^2, \end{aligned} \right\} \quad (4.11a)$$

where all distances $r = R/R_e$ are expressed in natural units, $v_1 = V/kT$, and v_3 is the fractional departure $n^-/N^- \exp(-V/kT)$ of the ion density from Boltzmann equilibrium. The first two coupled equations are equivalent to the Poisson equation (4.5), and the third equation represents diffusional drift (equation (4.9)).

When $v_1 \ll 1$ as at large r , the exponentials in (4.11a) may be linearized to provide

$$v_3 \approx 1 - \alpha/\alpha_h r \quad (4.11b)$$

so that the consistent and appropriate solution of the Poisson equation

$$\frac{1}{r} \frac{d^2(rv_1)}{dr^2} = \frac{1}{r_s^2} \left(v_1 + \frac{\alpha}{\alpha_h} \frac{1}{r} \right), \quad (4.11c)$$

$$v_1(r) = \frac{V}{kT} = -\frac{1}{r} \left(1 - \frac{1}{2\alpha_h} \right) \exp(-r/r_s) - \frac{\alpha/\alpha_h}{2r}, \quad (4.11d)$$

which yields the coulomb attraction (C) for $r \ll r_s$.

$$\text{At low } N, \quad v_1 \rightarrow -(1/r) \exp(-r/r_s), \quad (4.11e)$$

the Debye-Hückel interaction D.H. (cf. McDaniel 1964), while at large N when $\alpha \approx \alpha_h$,

$$v_1 \rightarrow -(1/2r)[1 + \exp(-r/r_s)] \quad (4.11f)$$

the mean of C and D.H. For intermediate N , v_1 contains various mixtures of C and D.H.

Direct numerical inward solution of (4.11a) subject to (4.11b) and (4.11d) as initial conditions at large r shows that (4.11d) remains an excellent solution by reproducing the actual numerical results to within 2% for all $r \geq 0.1$, for α/α_h between zero and unity and for $N^\pm \leq 10^{13} \text{ cm}^{-3}$. As α/α_h decreases from unity the accuracy becomes even better.

The criterion $v_1 \ll 1$ is satisfied at $r \sim 1$ (the important region at low N) and at small α/α_h when $r_s \gg 1$ which with (4.7), implies that $\frac{4}{3}\pi R_s^3 N^\pm = \frac{1}{2}r_s \gg 1$. Many ions are then present within the R_s -sphere, and $N^\pm \leq 2 \times 10^{14} \text{ cm}^{-3}$.

As N increases, the extent R_E of the reaction sink decreases as $(R_s/N)^{1/2}$ (see § 4.2), such that (4.11f) is pure coulomb at R_E in the high N -limit. For lower N , the situation is not as clear, without resort to explicit knowledge of the rate α of reaction.

4.2. Simplified method for reaction rate

Rather than solving the Boltzmann equation (2.20) directly for the phase-space densities $n_i(R, E_i)$ and hence α_{rn} from (2.50), let us adopt a procedure based on the analysis in § 2.4 of the finite reaction rate α_{rn} within a collisional sink of radial extent S . Since the X^+ and Y^- ions ($i = 1, 2$) have in general different mean free paths λ_i in the gas Z and since both ions have different sink radii R_i , the expression (2.84) or (2.91c) for the rate of reaction within S is therefore generalized to give

$$\alpha_{rn}(R_1, R_2) = \pi[R_1^2 W(X_1) C_1 E_1 + R_2^2 W(X_2) C_2 E_2 - R_m^2 W(Y_1) W(Y_2) G] \langle v_{12} \rangle, \quad (4.12a)$$

where $\langle v_{12} \rangle$ is some averaged ion-ion thermal or transport speed of approach, and where the probability for an ion i -neutral Z collision for ion pairs with internal separation $R \leq R_i$ increases with gas density to unity as (Loeb 1955)

$$W(X_i) = 1 - (1/2X_i^2) [1 - \exp(-2X_i)(1 + 2X_i)], \quad X_i = \lambda_i/R_i, \quad (4.12b)$$

for a straight-line trajectory. Since α_{rn} pertains to a Boltzmann distribution, the factor

$$E_i = \exp[-V(R_i + \lambda_i)/kT], \quad (4.12c)$$

in (4.12a) acknowledges the Boltzmann enhancement of the ion density N^- due to the field at $R_i + \lambda_i$ at which the last ineffective ion-neutral collision occurs just before the ion enters the recombination sink within R_i . The factor

$$C_i = 1 + \frac{2}{3kT} \int_{R_i}^{R_i + \lambda_i} \frac{\partial V}{\partial R} dR, \quad (4.12d)$$

acknowledges the focusing effect of the interaction on the assumed straight-line trajectory between $R_i + \lambda_i$ and R_i in the cross section πR_i^2 . The smaller of R_1 and R_2 is R_m such that $W(Y_1)W(Y_2)$, with $Y_i = \lambda_i/R_m$, is the probability of simultaneous ion-neutral collisions within R_m , a probability counted twice by the sum of the first two terms of (4.12a). Simple geometric arguments show that G in (4.12a) is equal to either $C_1 E_1$ or $C_2 E_2$ depending on whether R_m is equal to R_1 or R_2 , respectively.

The trapping radii R_i may now be deduced from simple kinematical considerations. The kinetic energy of (1, 2) relative motion before the i -Z collision is

$$T_b = \frac{3}{2}kT + \int_{R_i}^{R_i + \lambda_i} \frac{\partial V}{\partial R} dR, \quad (4.13)$$

since the ions on average are uninterrupted by collision only for separations between $R_i + \lambda_i$ and R_i , within which the acceleration due to the field is effective. Ion pairs upon collision with Z become incapable of expanding outwards from R_i to $R_i + \lambda_i$ provided their kinetic energy T_b after collision is barely sufficient for provision of the energy required to increase R_i to $R_i + \lambda_i$ against the force of attraction, i.e. when

$$T_b \leq \int_{R_i}^{R_i + \lambda_i} \frac{\partial V}{\partial R} dR. \quad (4.14)$$

We can show (Flannery 1978) from the full expression (Bates & Flannery 1968) for the energy change that, to a good approximation,

$$T_b = T_b(1 + \delta), \quad (4.15)$$

where δ is a parameter depending only on the masses M_i of the interacting species. Here we simply adopt δ as a convenient collision parameter chosen to normalize the low-density limit of the expression (4.12a) for α_{rn} to the exact quasi-equilibrium results of Bates & Flannery (1968). Thus, the stabilization criteria (4.14) with (4.13) yields

$$V(R_i + \lambda_i) - V(R_i) = \frac{3}{2}kT/\delta_i, \quad (4.16)$$

to be solved for the trapping radii R_i associated with mean free paths λ_i and collision parameters δ_i .

In this strong-collision model, (4.16) provides a valuable relation satisfied by the general interaction V at two points. Solution of (4.16) for a pure coulomb attraction is

$$R_i = \frac{1}{2}\lambda_i[(1 + 4\delta_i R_T/\lambda_i)^{1/2} - 1] \rightarrow \begin{cases} \delta_i R_T, & \text{as } N \rightarrow 0, \\ (\delta_i R_T \lambda_i)^{1/2}, & \text{as } N \rightarrow \infty, \end{cases} \quad (4.17)$$

which decreases monotonically as λ_i decreases from infinity and which is constrained by (4.16) to satisfy $R_i(R_i + \lambda_i) = \delta_i \lambda_i R_T$, where R_T is the Thomson trapping radius $2e^2/3kT$. The sink is therefore compressible with N , as in the model of Natanson (1959).

At low gas densities the reaction rate

$$\alpha_{rn} \rightarrow C_1 \delta_1^2 \alpha_{T1} + C_2 \delta_2^2 \alpha_{T2}, \quad (4.18)$$

where C_i , by (4.16), is $1 + \delta_i^{-1}$ and

$$\alpha_{T1} = \frac{4}{3}\pi R_T^2 \langle v_{12} \rangle / \lambda_i \quad (4.19)$$

is the Thomson partial recombination coefficient (1.3). The ratio

$$\mathcal{R}_{T1} = \alpha_{q.e.}(N \rightarrow 0) / \alpha_{T1} \quad (4.20)$$

of the exact low density limits $\alpha_{q.e.}$, as given by the quasi-equilibrium theory of Bates & Flannery (1968), has been provided (Flannery 1981a) for an extensive range of physical systems represented by



where energy-change transitions occur via elastic ion-neutral collisions. Also, the \mathcal{R}_{Ti} have been provided (Flannery 1980) for a wide range of systems represented by



where in addition to an elastic ($Y^- - X$) encounter a symmetrical resonance charge transfer encounter occurs, or by

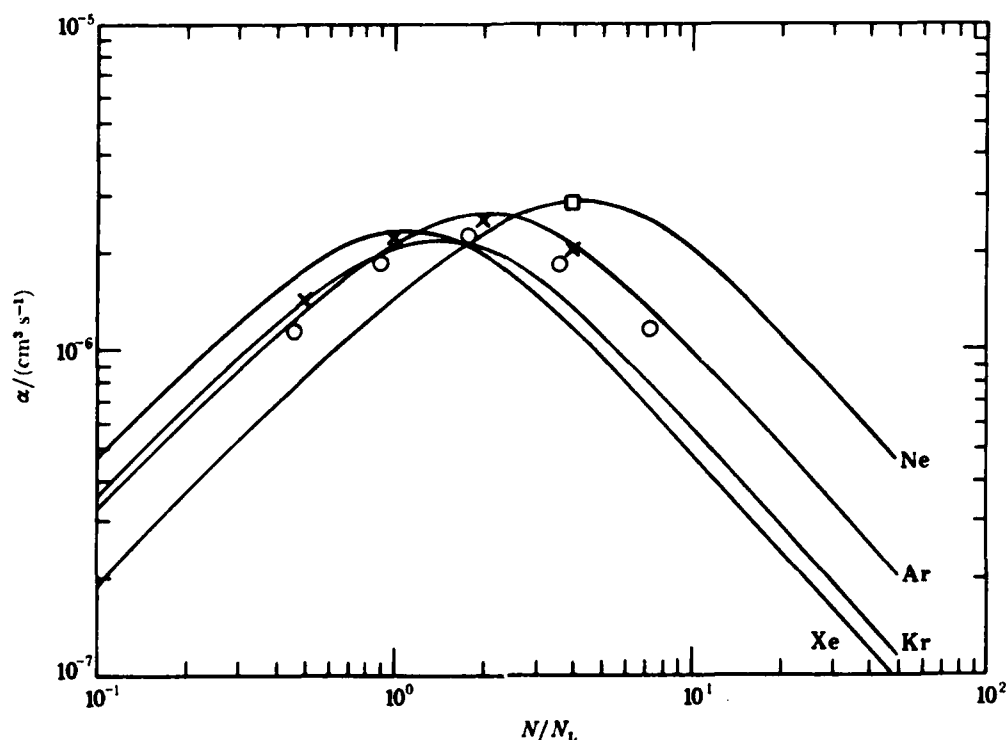


FIGURE 2. Recombination rate coefficient α at 300 K for $Kr^+ - F^-$ in rare gases (Ne, Ar, Kr, Xe) as a function of gas density N (in multiples of the Loschmidt number density $N_L = 2.69 \times 10^{19}$ at s.t.p.). —: Present treatment; \times , \square : universal Monte-Carlo (hard-sphere) plot (Bates 1980*b*) for Ar and Ne, respectively; \circ : Monte-Carlo (polarization) results (Morgan *et al.* 1980) for Ar.

With this knowledge, the collision parameters δ_i may now be uniquely determined by solution of

$$\delta_i^2 + \delta_i^2 - \mathcal{R}_{Ti} = 0, \quad (4.24)$$

and α_{rn} of (4.12*a*) tends therefore at low N to the exact quasi-equilibrium values (Flannery 1980, 1981*a*). This model of the reaction rate acknowledges the decrease in survival probability due to diffusion for ion-neutral collisions within the R_i -trapping spheres, and, with the inclusion of the quasi-equilibrium δ_i , is the 'strong-collision' analogue to the microscopic method provided in §3. The strong-collision parameter δ_i is, in general, a function of ion-density N^\pm .

4.3. Results for $[(Kr^+ - F^-) + M]$ recombination

For a pure coulomb interaction associated with dilute ionization, the collision parameters δ_i have been given (Flannery 1981*b*) for various combinations of rare gas (He^+ , Ne^+ , Ar^+ , Kr^+ , Xe^+) and halide (F^- , Cl^-) ions in a parent or unlike background gas M . In figure 2 are illustrated the variations of the rate

$$\alpha = \alpha_{rn} \alpha_{tr} / (\alpha_{rn} + \alpha_{tr}) \quad (4.25)$$

for the recombination of Kr^+ and F^- with density N of the background gas M , taken respectively as Ne, Ar, Kr and Xe, at 300 K. The reaction rate α_{rn} was obtained from (4.12), with (4.17) for R_i and the solution of (4.24) for δ_i , and the transport rate from

$$\alpha_{tr} = 4\pi e \{K_1/[1 - \exp(-R_e/R_1)] + K_2/[1 - \exp(-R_e/R_2)]\}. \quad (4.26)$$

Results from the universal Monte-Carlo plot procedure of Bates (1980*b*) are also shown in figure 2 together with the direct Monte-Carlo computer simulations of Morgan *et al.* (1980) at low N^\pm . The general agreement as shown can be considered excellent. At low N , $\alpha_{rn} \ll \alpha_{tr}$ while at high N , $\alpha_{rn} \gg \alpha_{tr}$ so that α is given by the rate-limiting step in each region. As N increases, α_{rn} increases with respect to α_{tr} until the maximum is obtained where $\alpha_{rn} \approx \alpha_{tr}$. Figure 2 can be made universal for all temperatures T by simply relabelling the ordinate and abscissa axes as $(T/300)^{1/2} \alpha$ and $(300/T)^{1/2} N$ respectively as pointed out by Bates (1980*c*). Analogous results for other systems are presented elsewhere (Flannery 1981*b*).

At higher N^\pm , the interaction between the ions varies in general with α , and is accurately determined by (4.11) which therefore must be coupled to the equation (whether basic as (2.52) or phenomenological as (4.12)) for α . At high gas densities ($N > \frac{1}{2}N_L$), Morgan *et al.* (1980) simply adopted *ab initio* the D.H. interaction (4.11*e*) as a means of incorporating plasma sheathing effects when N^\pm is raised. As shown in § 4.2 this assumption is without foundation unless $N \rightarrow 0$ and leads to greatly reduced rates which are in error particularly at intermediate and high gas densities N (Bates 1981, Flannery 1981*c*). Although increase in the ion density to about 10^{12} cm^{-3} is not expected to cause appreciable change (Flannery 1981*c*) to the rates of figure 2, direct calculation based on the theory of § 4.1 is under way.

5. THEORETICAL SOLUTION OF THE PHASE DENSITY

Since the phase-space density of ions in thermodynamic equilibrium separates quite naturally into a product of two functions—one of R alone and the other of v_i alone—as in (2.13), it remains convenient initially to express the set in terms of these natural (R, v_i) variables rather than (R, E_i) the set more natural for expression of the sink. Upon differentiation of (2.20) with respect to R or from (2.12) directly, we find with the aid of (2.10), that

$$v_i \left\{ 4\pi R^2 \frac{\partial}{\partial R} [N_i^*(R, v_i)/4\pi R^2] - \frac{4\pi v_i^2}{mv_i} \frac{\partial}{\partial v_i} [N_i^*(R, v_i)/4\pi v_i^2] \frac{\partial V}{\partial R} \right\} \\ = \int \int_{\Omega'} [N_i^*(R, v_i) N_0(\mathbf{v}_0') - N_i^*(R, v_i) N_0(\mathbf{v}_0)] [g\sigma(g, \psi) d\Omega] d\mathbf{v}_0 \quad (5.1a)$$

$$= N \left[\sum_{t=-M(R)}^C N_i^*(R, E_t) k_{ti}(R) - N_i^*(R, E_i) \sum_{t=-V(R)}^C k_{it}(R) \right], \quad (5.1b)$$

which is a set of linear integro-differential equations in two variables (rather than *quadratic* in $N_i(R, v_i)$ since the gas density $N_0(\mathbf{v}_0)$ has already been set in (5.1*b*) to its thermodynamic value, as implied by the condition $N^\pm \ll N_0$). The speeds v_0' and v_i in (5.1*a*) are given by energy conservation with fixed v_i , v_0 and Ω' . The recombination sink at internal energies below E_s requires that N_i^* vanishes for

$$v_i \leq v_{i0} = \{2/m[E_s - V(R)]\}^{1/2}, \quad R \leq R(E_s). \quad (5.2)$$

The equilibrium phase density (2.13) in (5.1) ensures that the left-hand side of (5.1) vanishes. This left-hand side includes the streaming (incompressible) terms while the right-hand side is the collisional integral that attempts to drive the momentum-space distribution of the system

towards a Maxwellian distribution. For small energy transfers the collision integral reduces (Flannery 1971, 1972) to that given by the Fokker-Planck equation (which essentially describes diffusion in momentum space) derived via description of recombination as a Markov process (Flannery 1971, 1972). For high gas densities and for high ion densities (more than several N_i) the decreased effect of accelerations and the increased ion-ion screening effect ensures respectively that the interaction $V \ll kT$ such that energy transfers are indeed small, such that the right-hand side of (5.1) is then best described by the Fokker-Planck equation.

For dilute ionization, $N^+ \ll N$, two new procedures are proposed with the above comments in mind for the solution $N_i^*(R, v_i)$ of (5.1) subject to certain boundary conditions.

5.1. Separable-equations method

In expression (5.1), let

$$N_i^*(R, v_i) = N_0(R, v_i) [1 - \Phi_i(R, v_i)], \quad (5.3)$$

in terms of the equilibrium density

$$N_0(R, v_i) = 4\pi R^2 \exp(-V/kT) F_0(v_i), \quad (5.4)$$

where the Maxwellian speed distribution is

$$F_0(v_i) = 4\pi v_i^2 (m/2\pi kT)^{3/2} \exp(-\frac{1}{2}mv_i^2/kT). \quad (5.5)$$

Since energy is conserved in the binary ion-neutral encounters,

$$N_0(R, v_i) N_0(v_0) = N_0(R, v_i') N_0(v_0'), \quad (5.6)$$

and hence, after some analysis, Φ_i satisfies the set

$$\begin{aligned} v_i \left[\frac{\partial}{\partial R} \Phi_i - \frac{1}{mv_i} \frac{\partial V}{\partial R} \frac{\partial \Phi_i}{\partial v_i} \right] &= \int \int_{\Omega} N_0(\mathbf{v}_0) [\Phi_i(R, v_i) - \Phi_i(R, v_i')] (g\sigma d\Omega) d\mathbf{v}_0 \\ &= N \left\{ \left[\sum_{t=-M(R)}^C \Phi_i(R, E_t) - \sum_{t=-N(R)}^C \Phi_i(R, E_t) \right] k_{it}(R) \right\} \end{aligned} \quad (5.7)$$

subject to the boundary conditions that

$$\begin{aligned} \Phi_i(R, E_i) &\rightarrow 0 \quad \text{for } E_i \rightarrow \infty, \quad \text{or for } R \rightarrow \infty \\ &\rightarrow 1 \quad \text{for } E_i \leq E_s, \quad R \leq R(E_s). \end{aligned} \quad (5.8)$$

In the limit of low gas densities N , the net rate of change of each of the streaming terms contained within all classical accessible configuration space between zero and $R_i(E_i)$, the outermost turning point, effectively balance, since the sink rate is small by comparison, i.e.

$$\int_0^{R_i} 4\pi R^2 \frac{\partial}{\partial R} \left[\frac{N_i^*(R, v_i)}{4\pi R^2} \right] dR \approx \frac{4\pi v_i^2}{m} \frac{\partial}{\partial v_i} \left[\frac{1}{4\pi v_i^2} \int_0^{R_i} N_i^*(R, v_i) \frac{\partial V}{\partial R} dR \right]. \quad (5.9)$$

The average rate over all accessible R -space of collisional transitions between levels with energies E_i and E_t can be written as,

$$\langle k_{it}(E_i, E_t) \rangle = \frac{1}{N_i^*(E_i)} \int_0^{R_i} N_i^*(R, E_i) k_{it}(E_i, E_t, R) dR, \quad (5.10)$$

where

$$N_i(E_i) = \int_0^{R_i} N_i^*(R, E_i) dR. \quad (5.11)$$

Hence, (5.1) reduces, with the aid of (5.9), to

$$N_1(E_1) \sum_{t=-D}^C \langle k_{1t}(E_1, E_t) \rangle = \sum_{t=-S}^C N_t(E_t) \langle k_{1t}(E_1, E_t) \rangle \quad (5.12)$$

which is the 'quasi-equilibrium' result of Bates & Moffett (1966) and of Bates & Flannery (1968) for ion densities N_1 appropriate to the limit of low gas densities N and valid when the left-hand side of (5.7) can be neglected.

As N is raised the first (spatial diffusion) term on the left-hand side of (5.7) becomes increasingly important while the second (acceleration) term eventually dominates in the high N -limit. Note, however, that *both* these terms must be included from the outset since their combination is required for thermodynamic equilibrium. Neglect of the acceleration term on the left-hand side of (5.1) does *not* yield, upon substitution of (5.3), the expression (5.7) with its acceleration term set to zero. Effects of diffusion and acceleration are so coupled that various schemes of approximation are best constructed from (5.7) as origin, rather than from (5.1).

For example, as N is raised, the speed distribution remains essentially Maxwellian while diffusion effects change, i.e. the correction Φ_1 in (5.3) to the Maxwell-Boltzmann distribution N_0 exhibits an R -variation alone. Hence the acceleration term in (5.7) can be neglected in comparison with the diffusion term, and with the substitution in (5.7) of

$$\Phi_1(R, v_1) = \Phi_1^1(R, v_1) \exp(-R/L_1), \quad (5.13)$$

$$\text{where the length} \quad L_1(v_1) \equiv L_1(R, E_1) = v_1/N \sum_t k_{1t}(R) \quad (5.14)$$

is a function only of v_1 (see Appendix B) then, after some analysis and reduction, Φ_1^1 satisfies the set of first-order coupled differential equations

$$\frac{\partial \Phi_1^1(R, E_1)}{\partial R} = \frac{N}{v_1} \sum_{t=-M(R)}^C \Phi_t^1(R, E_t) k_{1t}(R) \exp[-R(L_1^{-1} - L_t^{-1})], \quad (5.15)$$

which, by standard numerical techniques, can be solved easily subject to the boundary conditions (5.8).

The above set exhibits a striking similarity to the time-dependent set obtained in collision treatments based on Dirac's method of variation of constants (cf. Bates 1961). In fact, perturbation procedures based on the strength of the coupling terms k_{1t} result in a full hierarchy of computational schemes of varying degrees of sophistication. For example, the $\{k_{1t}\}$ -matrix is dominated by its diagonal (elastic) elements (cf. Flannery 1981a) such that to zero-order the non-diagonal elements are neglected, to give

$$\frac{\partial \Phi_1^1}{\partial R} \approx \frac{\partial \Phi_1^{(0)}}{\partial R} = \frac{N}{v_1} k_{11}(R) \Phi_1^{(0)} \quad (5.16)$$

with solution

$$\Phi_1^{(0)}(R, v_1) = \exp\left[-\frac{N}{v_1} \int_0^R k_{11}(R) dR\right]; \quad v_1(R) \geq v_{10} \quad (5.17)$$

which ensures that $N_1(R=0, v_1)/N_0(R=0, v_1)$ in (5.3) vanishes.

In this approximation, the phase density is

$$N_1^1(R, E_1) = N_0(R, v_1) \left\{ 1 - \exp\left[-RN \sum_t k_{1t}(R)/v_1\right] \exp\left[-N \int_0^R k_{11}(R) dR/v_1\right] \right\}, \quad (5.18)$$

which tends to N_0 as $R \rightarrow \infty$. It is worthwhile noting, even for approximation (5.18), that α given by (2.52) predicts a general nonlinear variation with gas density N for which the acceleration term in (5.7) can be neglected. Since off-diagonal terms are also ignored in this approximation to Φ_1^I , there is no coupling with the sink, and (5.18) is valuable only in providing interesting insight to the manner in which the diffusion term on the left-hand side of (5.7) affects the R -distribution of ion pairs. Full coupling with the sink is provided only by solution of the full set of coupled equations (5.15).

In the limit of high N , (5.18) predicts zero α , and the diffusion (R -gradient) term in (5.7) may therefore be neglected in comparison with the acceleration (v_1 -gradient) term. With the substitution

$$\Phi_1(R, v_1) = \Phi_1^{II}(R, v_1) \exp(v_1/V_1), \quad (5.19)$$

where the effective speed is

$$V_1(R, E_1) = \left(\frac{\partial V}{\partial R} \right) / mN \sum_i k_{it} \equiv a(R) \tau_1(R, E_1), \quad (5.20)$$

in terms of the acceleration $a(R)$ and of time $\tau_1 \equiv L_1(v_1^2)/v_1$ between collisions, the set (5.7), with diffusion ignored, yields, after some analysis and reduction, the set of first-order coupled differential equations

$$\frac{\partial \Phi_1^{II}(R, E_1)}{\partial v_1} = -\frac{N}{a(R)} \sum_{t=-\infty}^{\infty} \Phi_1^{II}(R, E_1) k_{it}(R) \exp[(v_t/V_t) - (v_1/V_1)] \quad (5.21)$$

analogous to the previous set (5.15). This set can also be solved to various degrees of sophistication. As before, the zero-order approximation follows by neglect of the off-diagonal elements to yield,

$$\frac{\partial \Phi_1^{II}}{\partial v_1} \approx \frac{\partial \Phi_1^{(0)}}{\partial v_1} = -\frac{N}{a(R)} k_{11}(R) \Phi_1^{(0)}, \quad (5.22)$$

such that

$$\Phi_1^{(0)}(R, v_1) = \exp \left[-\frac{N}{a(R)} \int_0^{v_1} k_{11}(R) dv_1 \right], \quad (5.23)$$

which vanishes as $R \rightarrow \infty$. Hence in this approximation the phase density is

$$N_1^{II}(R, E_1) = N_0(R, v_1) \left\{ 1 - \exp \left[Nm v_1 \sum_i k_{it} / \frac{\partial V}{\partial R} \right] \exp \left[-\frac{Nm}{\partial V / \partial R} \int_0^{v_1} k_{11}(R) dv_1 \right] \right\} \quad (5.24)$$

which exhibits an increasing or decreasing variation with N , depending on the kinetics of the collision.

For general N however, both diffusion and acceleration terms in (5.7) are effective. With the assumption that the first solution $\Phi_1^I(R, v_1)$ contains most of the R -variation and that $\Phi_1^{II}(R, v_1)$ contains most of the v_1 -variation, a working approximation for the general case (5.7) is

$$\Phi_1(R, v_1) \approx \frac{1}{2} (\Phi_1^I + \Phi_1^{II}), \quad (5.25)$$

where $\Phi_1^{I, II}$ are the full solutions of (5.15) and (5.21), respectively.

In the zero-order approximation that ignores the effect of the sink, we have

$$\begin{aligned} N_1^*(R, v_1) = N_0(R, v_1) & \left\{ 1 - \frac{1}{2} \exp(-NR \sum_i k_{it}/v_1) \exp \left(-\frac{N}{v_1} \int_0^R k_{11} dR \right) \right. \\ & \left. - \frac{1}{2} \exp \left[Nm v_1 \sum_i k_{it} / \frac{\partial V}{\partial R} \right] \exp \left[-\frac{Nm}{\partial V / \partial R} \int_0^{v_1} k_{11} dv_1 \right] \right\} \end{aligned} \quad (5.26)$$

which tends to N_0 when $R \rightarrow \infty$ or when $v_i \rightarrow \infty$. This 'one-channel' result is useful in providing insight into the overall effect of the diffusion and acceleration terms on the ion distribution. With (5.26) as a background density, various corrections may then be obtained. The effect of the sink is, of course, acknowledged by the full solution of (5.15) and (5.21).

Calculations based on the procedures outlined above are under way and will be presented in future reports.

5.2. 'Distribution in length between collisions' method: the frequency equation

The second and very effective approach for solution of (5.1) for the ion-phase densities is based on the recognition that the collisional integral, the right-hand side of (5.1), in contrast to the 'incompressible' streaming terms of the left-hand side, attempts via quasi-discontinuous collisions to drive the momentum-space part of the distribution towards Maxwellian at a given ion-ion separation R . With this in mind set the ion-pair distribution as,

$$N_i(R, v_i) = [4\pi R^2 \tilde{n}(R) N^+] F_0(v_i) [1 + \Phi_i(R, v_i)], \quad (5.27)$$

where $\tilde{n}(R)$ is some negative-ion configuration-space density yet to be determined, and where Φ_i , which represents the departure of the momentum distribution from the Maxwellian $F_0(v_i)$, will provide coupling to the recombination sink. On substituting (5.27) in (5.1), by noting that the acceleration term operating on the Maxwellian produces

$$-\frac{4\pi v_i^2}{m} \frac{\partial}{\partial v_i} \left[\frac{F_0(v_i)}{4\pi v_i^2} \right] = v_i F_0(v_i) \frac{\partial(V/kT)}{\partial R}, \quad (5.28)$$

after some reduction, we obtain (5.1) exactly as

$$\begin{aligned} v_i F_0(v_i) \left\{ \hat{D} \tilde{n}(R) + \frac{\partial}{\partial R} [\Phi_i \tilde{n}(R)] - \tilde{n}(R) \frac{\partial(V/kT)}{\partial R} \frac{\partial \Phi_i}{\partial T_i} \right\} \\ = \tilde{n}(R) F_0(v_i) \left[\iint_{\Omega} N_0(\mathbf{v}_0) (\Phi_i - \Phi_0) (g \sigma d\Omega) d\mathbf{v}_0 \right], \end{aligned} \quad (5.29)$$

where the \hat{D} -operator is such that

$$\hat{D} \tilde{n} \equiv \left[\frac{d}{dR} + \frac{d(V/kT)}{dR} \right] \tilde{n}(R), \quad (5.30)$$

and where T_i , the normalized kinetic energy of ion-ion relative motion is $\frac{1}{2} m v_i^2 / kT$. The separation of the collision integral (the right-hand side of (5.29)) into its various components suggests the solution

$$\Phi_i(R, v_i) = -[1/\tilde{n}(R)] \hat{D} \tilde{n}(R) l_i(v_i^2, R) \quad (5.31)$$

where l_i is an unknown function principally of v_i^2 , but only because of the recombination sink will depend, in general, on R and E_i . In thermodynamic equilibrium, Φ_i is zero and $\tilde{n}(R)$ is $N^- \exp(V/kT)$ such that $\hat{D} \tilde{n}$ vanishes. Hence the \hat{D} -operator in effect projects out the background R -variation due to outward diffusion and inward mobility and leaves only that R -variation due to the presence of the sink alone. When departures from thermodynamic equilibrium are not too strong we need not restrict $\hat{D} \tilde{n}$ to be small but its derivative $d(\hat{D} \tilde{n})/dR$ must vanish. Under this sole approximation (5.29) reduces with the aid of substitution (5.31), and after some analysis, to

$$v_i \left[1 - \frac{\partial l_i(v_i^2, R)}{\partial R} + \frac{\partial(V/kT)}{\partial R} \frac{\partial l_i(v_i^2, R)}{\partial T_i} \right] = N \left[l_i(R, E_i) \sum_{t=-V}^{\infty} k_{it}(R) - \sum_{t=-M}^{\infty} l_t(R, E_t) k_{it}(R) \right]. \quad (5.32)$$

The frequency ν_1 of ion-neutral collisions is

$$\nu_1(v_1) = N \sum_{t=-\infty}^{\infty} k_{it}(R), \quad (5.33)$$

such that the interval τ_1 between collisions for ions of speed v_1 is ν_1^{-1} and the mean length L_1 of their free paths is

$$L_1(v_1) = v_1 \tau_1 = v_1 / \nu_1. \quad (5.34)$$

When the ion-neutral collision cross section Q^E or Q^X for elastic or charge-transfer collisions is independent of the relative speed, the path length peculiar to speed v_1 is, as shown in the Appendix B,

$$L_1(v_1) = \pi^{1/2} X_1 / N Q^{X,E} [(2X_1 + 1)^{1/2} \pi^{1/2} \Phi_E(X_1^{1/2}) + X_1^{1/2} \exp(-X_1)], \quad (5.35)$$

where Φ_E is the error function which is a function of

$$X_1 = \frac{1}{2} M v_1^2 / kT \quad (5.36)$$

in terms of the reduced mass M of the ion-pair-neutral system. As $X_1 \rightarrow \infty$, $L_1 \rightarrow (NQ)^{-1} \equiv l_\infty$. Hence, (5.32) can be rewritten as

$$v_1 \left[\frac{l_1(R, E_1)}{L_1(v_1)} - 1 + \frac{\partial l_1(R, v_1^2)}{\partial R} - \frac{\partial(V/kT)}{\partial R} \frac{\partial l_1(R, v_1^2)}{\partial T_1} \right] = N \sum_{t=-\infty}^{\infty} l_t(R, E_t) k_{it}(R), \quad (5.37)$$

the basic equation to be solved for l_1 under appropriate boundary conditions.

The negative ion density n_1 is from (5.27) and (5.31) given by

$$n_1(R, E_1) = [\tilde{n}(R) - \hat{D} \tilde{n}(R) l_1(R, E_1)] F_0(v_1) \quad (5.38)$$

which tends to n_0 as $E_1 \rightarrow \infty$, i.e.

$$\tilde{n}(R) - \hat{D} \tilde{n}(R) l(R, \infty) = N^- \exp(-V/kT). \quad (5.39)$$

With use of (5.30) and an integrating factor, (5.39) is solved to yield

$$\tilde{n}(R) = N^- \exp(-V/kT) \exp[R/l(R, \infty)] \int_R^\infty \frac{\exp[-R/l(R, \infty)]}{l(R, \infty)} dR, \quad (5.40)$$

which tends to the appropriate thermodynamic value $N^- \exp(-V/kT)$ as $R \rightarrow \infty$. Hence, the overall phase density is

$$n_1(R, E_1) = N^- \exp(-V/kT) F_0(v_1) \left\{ \frac{l_1(R, E_1)}{l(R, \infty)} + \left[1 - \frac{l_1(R, E_1)}{l(R, \infty)} \right] H(E_1) \times \exp[R/l(R, \infty)] \int_R^\infty \frac{\exp[-R/l(R, \infty)]}{l(R, \infty)} dR \right\}, \quad (5.41)$$

where the Heaviside step function H is unity only for energies E_1 in the continuum (as implied by the $R \rightarrow \infty$ limit).

As $E_1 \rightarrow \infty$, (5.41) ensures that $n_1 \rightarrow n_0$; and as $R \rightarrow \infty$, $n_1 \rightarrow n_0$ implies that

$$l_1(R, E_1) \rightarrow l_1(\infty, E_1) = l(\infty, \infty) \equiv l_\infty. \quad (5.42)$$

Hence the set (5.37) is solved subject to the condition (5.42). As $E_1 \rightarrow \infty$, the right-hand side of (5.37) vanishes, $L_1 \rightarrow l_\infty$ and hence

$$\frac{l(R, \infty)}{l_\infty} - 1 + \frac{\partial l(R, \infty)}{\partial R} - \frac{\partial(V/kT)}{\partial R} \left[\frac{\partial l_1(R, E_1)}{\partial T_1} \right]_{T_1 \rightarrow \infty} = 0. \quad (5.43)$$

For infinite E_i or T_i , the last term on the left-hand side of (5.43) vanishes and the resulting equation can be solved, subject to the condition of vanishing $l_i(R \rightarrow 0, \infty)$, to give

$$l_i(R, \infty) = l_\infty [1 - \exp(-R/l_\infty)], \quad (5.44)$$

which satisfies (5.42) and which also ensures that $(\partial l_i / \partial R)_{R \rightarrow \infty}$ vanishes. Hence the phase density is given by (5.41) in terms of (5.44) and of $l_i(R, E_i)$, the solution of (5.37) over a spectrum of (R, E_i) -values subject to $l(R, \infty)$ as $E_i \rightarrow \infty$. Each solution will depend on the gas density N through l_∞ .

At high gas densities, $l_\infty \rightarrow 0$, $l(R, \infty) \rightarrow \infty$, and (5.41) tends to its thermodynamic equilibrium value, as expected. At low gas densities $l_\infty \rightarrow \infty$, and

$$l_i(R, E_i) \rightarrow l(R, \infty) \gamma(E_i), \quad (5.45)$$

where $\gamma(E_i)$ is a function only of E_i and is unity for $E_i \geq 0$. Hence (5.41) yields

$$n_i(R, E_i) = N \exp(-V/kT) F_0(v_i) \{\gamma(E_i) + [1 - \gamma(E_i)] H(E_i)\}. \quad (5.46)$$

The expression (5.37) for the distribution in the lengths $l_i(R, E_i)$ between collisions for use in (5.41) and hence in the recombination coefficient α in (2.52) is, apart from the neglect of $d[\hat{D}\tilde{n}(R)]/dR$ in (5.29), exact. The chief distinction between this proposed method and the previous method is that l_i is, in the absence of the recombination sink, a function only of v_i^2 , while Φ_i in (5.3) is a function of both R and v_i . Hence the R -dependence in $l_i(R, v_i^2)$ results only from the sink; the background R -dependence due to outward diffusion and mobility being acknowledged already by $\tilde{n}(R)$.

The physical meaning of the functions \tilde{n} and l_i in (5.27) and (5.31) becomes apparent by noting that the current density (ions $\text{cm}^{-2}\text{s}^{-1}$) is

$$J_s = \tilde{n}(R) \mathbf{v}_d = \int n_i(R, v_i) \mathbf{v}_i dv_i, \quad (5.47)$$

which with the aid of (5.27) and (5.31) reduces, after some analysis, to

$$J_s = -D_s \left[\frac{d\tilde{n}}{dR} + \tilde{n}(R) \frac{\partial(V/kT)}{\partial R} \right] \hat{\mathbf{R}} \quad (5.48)$$

where

$$D_s = \frac{1}{3} \int_{v_{i0}(R)}^{\infty} F_0(v_i) v_i l_i(v_i^2) dv_i \quad (\text{cm}^2\text{s}^{-1}) \quad (5.49)$$

is the diffusion coefficient in the presence of the sink for ions with the radial distribution $\tilde{n}(R)$. The factor of $\frac{1}{3}$ in (5.49) arises by adopting the radial direction $\hat{\mathbf{R}}$ as the Z -axis for v_i -integration of (5.47). Hence $l_i(v_i^2)$ is an actual path length at ion speed v_i (and not a phenomenological mean free path), such that the diffusion coefficient that would be measured in a recombination experiment is

$$D_s \equiv \frac{1}{3} \langle l_i v_i \rangle \quad (\text{cm}^2\text{s}^{-1}), \quad (5.50)$$

an average over the ion-distribution in the presence of the recombination sink. In light of this relation and of (5.34), the basic equation (5.37) which provides the average rate of increase of l_i between collisions can be referred to as *the frequency equation*.

As before, a hierarchy of approximate computational schemes can be proposed for evaluation of $l_i(R, E_i)$ from (5.37). Since $\tilde{n}(R)$ contains most of the background R -dependence, we can assume, with the aid of (5.44), that on the left-hand side of (5.32)

$$\frac{\partial l_i(R, v_i^2)}{\partial R} \approx \frac{\partial l(R, \infty)}{\partial R} = \exp(-R/l_\infty), \quad (5.51)$$

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RECOMBINATION AND CHEMICAL REACTIONS IN DENSE IONIZED
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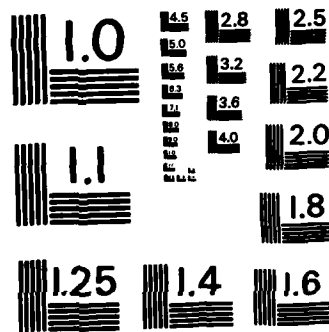
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and neglect initially the acceleration term $\partial(V/kT)/\partial R$. The resulting set of equations,

$$v_1 \left[\frac{l_1(R, E_1)}{L_1(v_1^2)} - 1 + \exp(-R/l_\infty) \right] = N \sum_{t=-M}^C l_t(R, E_t) k_{it}(R) \quad (5.52)$$

can be evaluated by normal computational techniques.

6. SUMMARY

In this paper a basic microscopic theory of ion-ion recombination as a function of gas density N has been presented. We have developed a basic equation (2.20), a *linear Boltzmann equation*, for the distribution in phase space of ion pairs, and have proposed in § 5 effective methods – the ‘separable-equations’ method and the ‘distribution in length between collisions’ method – for its steady-state solution. An expression (2.52) for the recombination coefficient α in terms of the phase-space distributions has been constructed from *the flux equation* (2.43), a combination of *the equation of continuity* (2.30) and of *the momentum equation* (2.36), both of which have been derived from basic microscopic principles, i.e. the macroscopic effects are truly addressed in language of their microscopic origins in the presence of the recombination sink.

An alternative expression (2.59) for α has been derived in terms of α_{rn} , the rate of reaction or, equivalently, the recombination coefficient that would pertain provided a Boltzmann distribution of ions were maintained, and of α_{tr} , the rate of ionic transport by diffusional drift. The steady-state recombination rate is determined at any gas density N by the rate-limiting steps of reaction and transport which proceed in series. This expression not only provides interesting insights into the internal workings of recombination, as in § 2.4, but is also very valuable when alternative means (as in § 4.2) are used to deduce reliable reaction rates α_{rn} alone, without the necessity of solving the linear Boltzmann equation (2.20). Further theoretical development of this expression reveals in § 3 an N -variation of α consistent with both the nonlinear rise at low N of Thomson’s expression, which therefore can be identified with the reaction rate, and with the N^{-1} -decrease in Langevin’s result which is the transport rate.

The basic time evolution of recombination is developed in § 2.4 where the Debye-Smoluchowski time-dependent equation (2.89), which is a natural consequence of the present basic theory, is solved for the time dependence of the density of ions undergoing diffusional drift in an arbitrary spherical potential and a reactive sink. This solution enables us to investigate analytically the explicit variation of the recombination rate $\alpha(t)$ with time. For an initial Boltzmann distribution, $\alpha(t)$ is initially determined by the reaction rate, as expected, and tends at large t ($\gg S^2/D$) to its steady-state limit determined by the limiting rate of reaction or transport. For $N \lesssim N_L$, a straight-line dependence of $\alpha(t)$ with t is noted, since the reaction rate is always much slower, while high $N > N_L$ produces the interesting effect of transition between reaction (initially) and transport, which are the two series components of recombination. This time variation is such that it would permit verification by techniques of modern laser spectroscopy and by appropriate Monte-Carlo computer experiments. Such time dependences will be very important in many applications ranging from medical radiology and biophysics to ionization tracks.

As $N \pm$ is raised, the ion-ion interaction V is, in general, obtained as described in § 4 from the self-consistent solution of the linear Boltzmann equation (2.20) for the phase-space densities, coupled to Poisson’s nonlinear equation (4.5) for the radial number densities. The recombination rate α can then be determined as a function of both N and $N \pm$. Otherwise, if the analytic reaction

rate α_{rn} is known in terms of V as in § 4.2, then Poisson's equation can be solved directly for V . Use of a model for α_{rn} has been illustrated for Kr^+-F^- recombination as a function of N for various rare gases.

In conclusion, basic theory has been presented here that thoroughly investigates the recombination rate as a function of gas density, ion density and time.

APPENDIX A. ANALOGY WITH CONDUCTING SPHERE

Introduce a single conducting sphere of radius S held at constant potential ϕ_S into a field of constant potential ϕ_0 . The potential ϕ at any point R from the centre of the sphere satisfies Laplace's equation,

$$\nabla^2 \phi = 0, \quad (A 1)$$

with solution
$$\phi(R) = \phi_0 [1 - (S/R) (1 - \phi_S/\phi_0)]. \quad (A 2)$$

The total charge induced on the sphere is

$$q_i = -\frac{1}{4\pi} \int \nabla \phi \cdot dS = -S\phi_0(1 - \phi_S/\phi_0). \quad (A 3)$$

For recombination, the steady-state diffusional-drift current j towards a central positive ion satisfies (2.68), i.e.

$$\nabla \cdot j = \nabla \cdot [D \exp(-V/kT) \nabla n^- \exp(V/kT)] = 0, \quad (A 4)$$

subject to $n = N^-$ at infinity and to $n = n_S$ at the surface of the sink of radius S , respectively. When the field V is neglected, the resulting Laplace's equation is solved to give the density

$$n^-(R) = N^- [1 - (S/R) (1 - n_S/N^-)]. \quad (A 5)$$

The flux across any R -sphere is,

$$F^- = 4\pi S D (1 - n_S/N^-) N^- \equiv \alpha_d (1 - n_S/N^-) N^- = \alpha N^-, \quad (A 6)$$

where α_d is the recombination rate α appropriate to instantaneous reaction ($n_S = 0$). Analogy with electrostatics then follows by identifying the local ion density n^- with the local potential ϕ , and the flux of ions across S with the induced charge. Hence, the recombination rate α is equivalent to $4\pi D$ times the 'induced charge q_i ' per unit 'external potential ϕ_0 ', and the transport rate α_d is $4\pi D$ times the 'induced charge q_i ' per unit 'potential difference ($\phi_S - \phi_0$)'. Introduce a reaction rate α_3 at S by

$$\alpha_3 n_S = \alpha N^-, \quad (A 7)$$

which equates the incident flux with the rate (s^{-1}) of reaction. Thus the reaction rate α_3 is $4\pi D$ times the 'induced charge q_i ' per 'unit surface potential ϕ_S '. Thus α , α_3 and α_d may be regarded as appropriate capacitances of the sphere associated with potentials ϕ_0 , ϕ_S and $\phi_S - \phi_0$, respectively. From (A 6) and (A 7),

$$1/\alpha = 1/\alpha_3 + 1/\alpha_d, \quad (A 8)$$

showing that the overall rate ($cm^3 s^{-1}$) is equivalent to a capacitance associated with potential ϕ_S joined in series to a capacitance with potential $\phi_S - \phi_0$. This analogy is similar in spirit to that of Bates (1974).

For non-zero V , (A 4) can be reduced to Laplace's equation (A 1) via transformations (2.105) and (2.107). The above analogy between ϕ in (A 1)–(A 3) and $n \exp(V/kT)$ is preserved in R -space. The equivalent solution is then

$$n^-(R) = N^- \exp(-V/kT) \{1 - (S/R) (1 - n_S \exp[V(S)/kT]/N^-)\}, \quad (A 9)$$

which is analogous with (A 2). With the aid of (2.105), the inward flux across any R -sphere is

$$F^- = 4\pi R^2 D \exp(-V/kT) [dn(R) \exp(V/kT)/dR] \quad (\text{A } 10)$$

$$= 4\pi D N^- \bar{S} \{1 - (n_+/N^-) \exp[V(S)/kT]\}, \quad (\text{A } 11)$$

such that, with (A 7), $1/\alpha = 1/\alpha_{rn} + 1/\alpha_{tr}$ (A 12)

where the diffusional-drift transport rate that replaces α_d is

$$\alpha_{tr} = 4\pi \bar{S} D \equiv 4\pi D \int_S^\infty \exp(V/kT) R^{-2} dR \quad (\text{A } 13)$$

as in (2.115), and where the reaction rate is

$$\alpha_{rn} = \alpha_3 \exp[-V(S)/kT]. \quad (\text{A } 14)$$

This analogy may be extended to cover the case where there are many non-overlapping conducting and identical spheres. A charge on one reference sphere induces on the remaining spheres an image charge that can be replaced by an induced charge and a dipole located at each centre. A self-consistent set of charges and dipoles are set up. The recombination coefficient pertinent to a large number of positive ions is then given by $4\pi D$ times the self-consistent 'induced charge' per unit potential ϕ_0 at infinity. This analogy furnishes a method whereby the competition for flux between the various non overlapping sinks can be acknowledged and is therefore relevant to the case of high ion density.

APPENDIX B. THE PECULIAR MEAN FREE PATH

The path length of an ion moving with speed v_1 in a gas of density N is defined by equation (5.14) as

$$L_1(v_1) = v_1 / [N \sum_i k_{it}(R)], \quad (\text{B } 1)$$

where the denominator is the frequency ν_1 for all elastic ion-neutral collisions that leave an R -ion pair in all states of binding (bound and dissociative) at fixed internal separation R . Thus, the collisional rate ($\text{cm}^3 \text{s}^{-1}$) between an ion i and a gas atom 3 is

$$\sum_i k_{it}(R) \equiv \int_{-\infty}^{\infty} k'(E_i, E_t, R) dE_t = \frac{1}{2} \int_0^\infty G(v_3) dv_3 \int_\Omega g \sigma(g, \psi) d(\cos \psi) d\phi \int_{-1}^{+1} d\mu, \quad (\text{B } 2)$$

where $g = v_1 - v_3$; $\mu = \hat{v}_1 \cdot \hat{v}_3$ (B 3)

and where G is the distribution of gas speeds v_3 . The differential cross section for i -3 scattering in the i -3 centre-of-mass reference frame is σ , which for isotropic (hard-sphere) scattering independent of the (thermal) impact speed is $Q/4\pi$ in terms of the integral cross section Q . Hence

$$\begin{aligned} \sum_i k_{it}(R) &= Q \int_0^\infty G(v_3) dv_3 (v_1 + \frac{1}{2} v_3^2 / v_1), \quad v_1 > v_3, \\ &= Q \int_0^\infty G(v_3) dv_3 (v_3 + \frac{1}{2} v_1^2 / v_3), \quad v_1 < v_3, \end{aligned} \quad (\text{B } 4)$$

which reduces, for a Maxwellian distribution with respect to the centre of mass of the ion pair, to

$$\sum_i k_{it}(R) = \frac{1}{2} Q \langle v_3 \rangle [(2X_1^{\frac{1}{2}} + X_1^{-\frac{1}{2}}) \frac{1}{2} \pi^{\frac{1}{2}} \Phi_E(X_1^{\frac{1}{2}}) + \exp(-X_1)], \quad (\text{B } 5)$$

where $X_1 = (\frac{1}{2} M v_1^2 / kT)$ (B 6)

in terms of the reduced mass M of the (ion-pair-gas) system, where

$$\Phi_E(X_1^{\frac{1}{2}}) = \frac{2}{\sqrt{\pi}} \int_0^{X_1^{\frac{1}{2}}} \exp(-t^2) dt = \frac{1}{\sqrt{\pi}} \int_0^{X_1} E^{-\frac{1}{2}} \exp(-E) dE, \quad (\text{B } 7)$$

is the probability integral (or error function), and where $\langle v_3 \rangle$ is the mean thermal speed $(8kT/\pi M)^{\frac{1}{2}}$ of the gas atoms. The total rate (B 5) tends to $Q \langle v_3 \rangle$ and to $Q v_1$ as $v_1 \rightarrow 0$ and as $v_1 \rightarrow \infty$, respectively. Equation (5.35) for L_1 in the text is therefore recovered from (B 1) and (B 5.)

We note that

$$L_1(v_1)/L_1(\infty) = \pi^{\frac{1}{2}} X_1 / [(2X_1 + 1)^{\frac{1}{2}} \pi^{\frac{1}{2}} \Phi_E(X_1^{\frac{1}{2}}) + X_1^{\frac{1}{2}} \exp(-X_1)], \quad (\text{B } 8)$$

increases monotonically with v_1 from zero to unity. The results (B 5) and (B 8) hold for either elastic or charge-transfer ion-neutral collisions with cross sections Q assumed to be independent of the relative speed.

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Appendix G

Analytical Solutions of the Debye-Smoluchowski Equation for Geminate and Homogeneous Recombination and for Fluorescence Quenching, Phys. Rev. A 25, 3404-3406 (1982).

Analytical solution of the Debye-Smoluchowski equation for geminate and homogeneous recombination and for fluorescence quenching

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Closed-form analytical time-dependent solutions of the Debye-Smoluchowski equation with a general spherical interaction are obtained for the important cases of geminate and homogeneous recombination by diffusional drift in a gas or liquid medium. A relationship between the time-dependent probability for recombination or escape in geminate recombination and the transient rate for homogeneous recombination is established. An expression for the rate of decay of emitted intensity in fluorescence quenching is also derived.

When a dissociated pair A and B is generated instantaneously within a gas or liquid medium then the $(A-B)$ pair may react internally or escape by diffusional drift in the presence of a sink to infinite separation. The key quantity in this *geminate recombination* process is the probability $\mathcal{P}(t)$ or $\Sigma(t)$ for recombination or survival, respectively, of the dissociating pair at time t . When reaction occurs between a central species A and another of the species B created within the medium by a continuous source at infinity (or else by escape from geminate recombination), then this recombination is *homogeneous* and is characterized by an effective two-body coefficient $\alpha(t)$ cm^3s^{-1} appropriate to termolecular reactions. Contact has recently been established¹ between the basic microscopic (phase-space) theory of chemical reactions influenced by diffusional drift in a medium and the (Debye-Smoluchowski) macroscopic equation of continuity

$$-\frac{\partial n}{\partial t}(R,t) + \vec{\nabla} \cdot \vec{J}_l(R,t) = \alpha_3 n \delta(\vec{R} - \vec{S}) \quad (1)$$

for the probability density $n(R,t)$ for finding an AB pair with internal separation $R \geq S$. Here α_3 is the local rate of reaction (via three-body AB collisions with the medium) for AB pairs brought to internal separation S by the diffusional-drift current $\vec{J} = -\vec{J}_l$ with

$$\begin{aligned} \vec{J}_l(R,t) &= D \vec{\nabla} n(R,t) + (K/e) n(R,t) \vec{\nabla} V(R) \quad (2a) \\ &\equiv D [\exp(-V/kT) \vec{\nabla} n(R,t) \exp(V/kT)] \end{aligned}$$

(2b)

expressed as a generalized Fick's law by use in (2a) of the Einstein relation ($De = K kT$) between the diffusion coefficient D (cm^2s^{-1}) and mobility K ($\text{cm}^2/\text{statvolt s}$) for relative AB motion in the gas or liquid medium. Equation (1) is equivalent to the corresponding homogeneous equation solved subject to the partially absorbing boundary condition

$$4\pi S^2 J_l(S,t) = \alpha_3 n(S,t) \quad (3)$$

which assumes that the net inward radial diffusional-drift current at S is absorbed by reaction within S .

It has recently been shown¹ how analytical time-dependent solutions of (1) for an arbitrary spherical interaction can, in general, be obtained in closed form via introduction of the transformation¹ from the variable R to

$$\tilde{R} = \left[\int_R^\infty \exp(V/kT) R^{-2} dR \right]^{-1} \quad (4)$$

which then reduces (1) to a form capable of exact solution for $R \geq$ the natural unit (n.u.) at which the thermal (kT) and potential (V) energies are equal. It is the purpose of this communication to briefly summarize the key results obtained for geminate and homogeneous recombination. Recombination is used here in its most general sense of any chemical reaction influenced by diffusional drift in a gas or liquid (electron-ion and ion-ion neutralization, coagulation of colloids, electrolytic reactions, chemical conversions, etc.).

On setting

$$n'(\bar{r}, \tau) = \frac{\bar{R}}{\bar{S}} n(R, t) \exp V(R)/kT;$$

$$\bar{r} = \frac{\bar{R}}{\bar{S}} - 1,$$

$$\tau = Dt/S^2 \quad (5)$$

then the homogeneous equation corresponding to (1) reduces to

$$\begin{aligned} \frac{\partial n'}{\partial \tau}(\bar{r}, \tau) &= \left[\frac{d\bar{r}}{d\tau} \right]^2 \frac{\partial^2 n'}{\partial \bar{r}^2}(\bar{r}, \tau) \\ &= \frac{\partial^2 n'}{\partial r^2} + \left[\left[\frac{d\bar{r}}{d\tau} \right]^2 \frac{d^2 r}{d\bar{r}^2} \right] \frac{\partial n'}{\partial r} \end{aligned} \quad (6)$$

which suggests the following two procedures for solution: Assume $(d\bar{r}/d\tau)$ remains constant such that introduction of

$$\bar{\tau}(\tau) = \left[\frac{d\bar{r}}{d\tau} \right]^2 \tau \quad (7a)$$

in (6) yields²

$$\frac{\partial n'}{\partial \bar{\tau}}(\bar{r}, \bar{\tau}) = \frac{\partial^2 n'}{\partial \bar{r}^2}(\bar{r}, \bar{\tau}) \quad (7b)$$

which is the field-free diffusion equation in $(\bar{r}, \bar{\tau})$ space. Alternatively, since the coefficient on the right hand side of (6),

$$\begin{aligned} \left[\frac{d\bar{r}}{d\tau} \right]^2 \frac{d^2 r}{d\bar{r}^2} &= -S \left[\frac{2\bar{R}}{R^2} \exp(V/kT) - \frac{2}{R} \right. \\ &\quad \left. + \frac{\partial}{\partial R}(V/kT) \right] \end{aligned} \quad (8a)$$

vanishes to $O(R^{-3})$ for the Coulomb interaction and is negligible for $R^3 \geq SR_e^2 \equiv S(e^2/kT)^2$, then

$$\frac{\partial n'}{\partial \tau}(r, \tau) = \frac{\partial^2 n'}{\partial r^2}(r, \tau), \quad (8b)$$

the one-dimensional diffusion equation in (r, τ) space. The radiation boundary condition (3) in cases (7b) and (8b) is

$$\left[\frac{\partial n'}{\partial \bar{r}} \right]_0 = \left[\frac{\alpha_{RN}}{\alpha} \right] n'(0, t) \quad (9a)$$

or

$$\left[\frac{\partial n'}{\partial r} \right]_0 = \frac{\alpha_{RN}}{\alpha} \left[\frac{\bar{S}}{S} \exp \frac{V(S)}{kT} \right] n'(0, t), \quad (9b)$$

respectively, where

$$\alpha = \frac{\alpha_{RN} \alpha_{TR}}{\alpha_{RN} + \alpha_{TR}} \quad (10a)$$

in terms of the reaction rate at S ,

$$\alpha_{RN} = \alpha_3 \exp[-V(S)/kT] \quad (10b)$$

at S , and of the transport rate at S :

$$\alpha_{TR} = 4\pi D \bar{S}. \quad (10c)$$

When $\alpha_{RN} \gg \alpha$, as at high N , then (9a) implies full absorption with zero $n'(0, t)$ and when $\alpha_{RN} \ll \alpha$, as a low N , then (9a) implies partial absorption with zero $(\partial n'/\partial \bar{r})_0$.

For geminate recombination, the solution of (1), subject to the initial condition

$$n(R, t=0) = \mathcal{N}_0 \delta(R - R_0)/4\pi R_0^2 \quad (11a)$$

for instantaneous generation of $\mathcal{N}_0 \equiv \mathcal{N} \exp[-V(R_0)/kT]$ species A at a fixed distance R_0 from the central, and subject to the boundary condition

$$n(R \rightarrow \infty, t) = 0 \quad (11b)$$

is determined from (8b) and (9b) to be

$$\begin{aligned} n(R, t; R_0, S) &= \frac{\mathcal{N} \exp(-V/kT) \bar{R}_0}{(4\pi R_0^2)(4Dt)^{1/2} \bar{R}} \\ &\quad \times \left[\frac{1}{\sqrt{\pi}} [\exp(-\Omega_0^2) + \exp(-\Omega_1^2)] \right. \\ &\quad \left. - 2\chi \exp(\chi^2) \exp(2\Omega_1 \chi) \operatorname{erfc}(\chi + \Omega_1) \right] \end{aligned} \quad (12a)$$

in terms of (4), and of the dimensionless quantities

$$\Omega_0(R, t) = \frac{(R - R_0)}{(4Dt)^{1/2}}, \quad \Omega_1(R, t) = \frac{(R + R_0 - 2S)}{(4Dt)^{1/2}},$$

$$\chi(t) = \left[\frac{\alpha_{RN}}{\alpha} \right] \left[\frac{Dt}{S^2} \right]^{1/2} \frac{\bar{S}}{S} \exp[V(S)/kT]. \quad (12b)$$

For homogeneous recombination, the solution of (1) subject to the initial and boundary conditions

$$\begin{aligned} n(R, t=0) &= N_0 \\ n(R \rightarrow \infty, t) &\rightarrow N_0 \exp[-V(R)/kT] \end{aligned} \quad (13)$$

of a Boltzmann equilibrium distribution, is similarly

$$n(R, t) = N_0 \exp(-V/kT) \times \left[1 + \frac{\alpha}{\alpha_{TR}} \frac{\tilde{S}}{\tilde{R}} \times [\exp(2\Omega\chi) \exp\chi^2 \operatorname{erfc}(\chi + \Omega) - \operatorname{erfc}\Omega] \right], \quad (14a)$$

where $\chi(t)$ is defined in (12b), and where

$$\Omega(R, t) = \frac{(R - S)}{(4Dt)^{1/2}} \equiv \frac{(\tilde{R} - \tilde{S})}{(4Dt)^{1/2}} \left[\frac{dR}{d\tilde{R}} \right], \quad (14b)$$

since $(d\tilde{R}/dR)$ is assumed constant. The solutions (12a) and (14a) are exact at all times over the region $R^3 \geq R_{\min}^3 = SR_e^2$ where (8a) can be assumed negligible and therefore hold over the relevant range $R \geq S$ when $S \geq R_e$. The steady-rate solutions obtained from (7b) are exact over all R and are identical with the $(t \rightarrow \infty)$ limit of (12a) and (14a). Both methods based on (7b) and (8b), respectively, yield results which become identical when $[\tilde{R}/(d\tilde{R}/dR)]$ is replaced by R , as in (14b). The actual diffusion coefficient D in (2) has also been assumed constant, an assumption which depends on the density of the medium and therefore valid³ when $R \geq 3R_e$, R_e , and $0.2R_e$ at 0.1, 1, and 20 atm, respectively, for Coulombic attraction.

The survival probability that each AB pair has not reacted in geminate recombination,

$$\Sigma(t) = \frac{1}{N_0} \int_{\mathcal{V}} n(R, t; R_0, S) d\tilde{R}, \quad (15a)$$

where the integration is over all volume \mathcal{V} external to the surface \mathcal{S} of the spherical sink, is best evaluated indirectly from

$$\Sigma(t) = 1 - \mathcal{P}(t) = 1 - \frac{1}{N_0} \int_0^t \nu(t) dt, \quad (15b)$$

where the frequency of recombination is

$$\nu(t) = - \int_{\mathcal{S}} \left[\frac{\partial n}{\partial t} \right] d\tilde{R} = \alpha_3 n(S, t; R_0, S) \quad (15c)$$

since J_i vanishes at infinity and within \mathcal{S} .

Without loss of generality, a coincident source and sink ($R_0 \approx S$) can be assumed in (15b) with (15c) and (12a), so that the recombination probability is

$$\mathcal{P}(t) = \frac{\alpha}{\alpha_{TR}} [1 - \exp\chi^2(t) \operatorname{erfc}\chi(t)] \quad (15d)$$

which tends at long times $t \gg S^2/D$ to $\alpha_{RN}/(\alpha_{RN} + \alpha_{TR})$. From the rate of decrease in the number of diffusional-drift species outside S the rate coefficient $\alpha(t)$ for homogenous recombination is

$$\alpha(t) = - \frac{1}{N_0} \left[\frac{d}{dt} \int_{\mathcal{V}} n(R, t) d\tilde{R} - \mathcal{F}_{\infty} \right] = \alpha_3 n(S, t) / N_0, \quad (16)$$

where \mathcal{F}_{∞} is the net inward flux generated continuously at infinity. With the aid of (14a),

$$\alpha(t) = \alpha \left[1 + \left[\frac{\alpha_{RN}}{\alpha_{TR}} \right] \exp\chi^2(S, t) \operatorname{erfc}\chi(S, t) \right]. \quad (17)$$

From (15d), (17), and (10a), we obtain

$$\alpha(t) = \alpha_{RN} \Sigma(t) \rightarrow \alpha_{TR} \mathcal{P}(\infty) \quad (18)$$

between the transient rate $\alpha(t)$ for homogeneous recombination and the transient recombination and escape probabilities $\mathcal{P}(t)$ and $\Sigma(t)$, respectively.

When instantaneous generation of A occurs at $R_0 = S$, i.e., reaction may immediately follow, then the fractional number of A that can be found at time t within a spherical shell of thickness dR and centered at B is

$$\mathcal{F}(R, t) dR = 4\pi R^2 n(R, t; S, S) dR / N_0, \quad (19)$$

for geminate recombination.

Figure 1 is a three-dimensional display of the variation of $\mathcal{F}(R, t)$ with both interseparation R [in units of the natural length (e^2/kT) and in intervals of 0.05 from $R = 1.0$, the assumed radius of the sink, to $R = 2.2$] and time t (in units of S^2/D and in intervals of 0.05 from 0.05 to 0.70) for geminate recombination between positive and negative ions. Here equal rates of transport and reaction are assumed such that $\mathcal{P}(\infty)$ and $\Sigma(\infty)$ equal 0.5. Each approximately right-to-left curve provides the fixed- R variation of $\mathcal{F}(R, t)$ with t while each left-to-right curve provides the fixed-time variation of $\mathcal{F}(R, t)$ with R . The boundary curve $\mathcal{F}(S, t)$ provides the variation with time of the recombination frequency $\nu(t)$ which decreases to zero as expected. This figure is a striking illustration of the evolution with time and separation of an ion pair subject to reaction and diffusional drift, i.e., of the geminate recombination process.

Figure 2 displays the time variation of the probability (15d) for geminate recombination. The initial variation $\sim 0.5 (1 - 1.3\tau^{1/2})$ at short times is

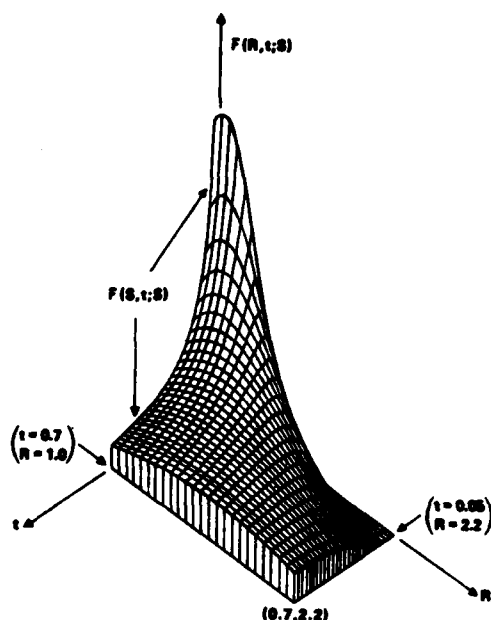


FIG. 1. Evolution of the fractional number $\mathcal{F}(R, t; S)$ of ion pairs per unit dR interval with time t [in units of (S^2/D)] and with internal separation R (in units of $R_0 = e^2/kT$) appropriate to equal rates α_{TR} and α_{RN} of transport and reaction, respectively, at a sink of radius $S = 1.0(R_0)$.

rapid in comparison with that $\sim 0.5(1 - 0.5\tau^{-1/2})$ at asymptotic times. The bulk of the probability for geminate recombination (19) is achieved effectively instantaneously within a few S^2/D (e.g., \mathcal{P} increases to 0.3 and 0.4 at $\tau=1$ and 5, respectively), a feature apparent also for the homogeneous case² with an initial Boltzmann distribution and continuous source of ionization, particularly for low gas densities. Fluorescence quenching of excited fluorophores A^* of density $n_A(t)$ after an initial incident laser pulse of excitation is governed by

$$\frac{dn_A(t)}{dt} = -[\tau_A^{-1} + \alpha(t)n_B(t)]n_A(t), \quad (20)$$

$$n_A(t) = n_A(0) \exp \left[-t/\tau_A - \int_0^t \alpha(t)n_B(t)dt \right], \quad (21)$$

where τ_A is the unquenched radiative lifetime of A^* and where n_B is the density of the quenching

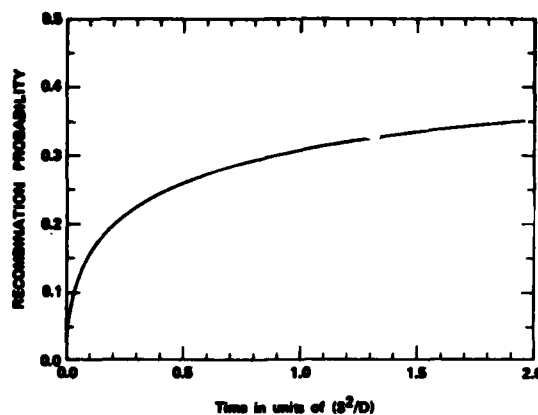


FIG. 2. Variation of the probability for geminate ion-ion recombination with time appropriate to the case of Fig. 1.

species B with an initial Boltzmann distribution.

If the quenching species B are chemically inert or if $n_B \gg n_A$, then n_B is effectively constant. With $\alpha(t)$ given by (17), the integral

$$\int_0^t \alpha(t)dt = \alpha t \left[1 + \left[\frac{\alpha_{RN}}{\alpha_{TR}} \right] \chi^{-2} \left[\exp \chi^2 \operatorname{erfc} \chi - (1 - 2\chi/\sqrt{\pi}) \right] \right] \quad (22)$$

which varies as $\alpha_{RN}t[1 - O(t^{1/2})]$ and as $\alpha t[1 - O(t^{-1/2})]$ at short and long times, respectively. Thus the decay law (21) is known exactly at all times. Note that the collisional quenching part of $n_A(t)$ decreases initially as $\exp(-\alpha_{RN}t)$ and after long times as $\exp[-\alpha(\infty)t]$, as expected. The full transient fluorescence is governed by (21) and (22) which is capable of experimental verification for any fluorophor-quencher system in a gas or liquid medium.

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¹M. R. Flannery, Philos. Trans. R. Soc. London, Ser. A **304**, 447 (1981).

²A. R. Flannery, Phys. Rev. Lett. **47**, 163 (1981).

... is constant when the electric-field inten-

sity E divided by the gas density $N \lesssim 20 \times 10^{-17} \text{ cm}^2/\text{V}$, i.e., for a Coulomb attraction then $R \geq S_m = (0.85N_L/N)^{1/2}(T/300)R_0$, where N_L is $2.69 \times 10^{19} \text{ cm}^{-3}$.